

# Supporting Information

## Synthesis of Primary and Secondary Alkylboronates through Site-Selective C(sp<sup>3</sup>)–H Activation with Silica-Supported Monophosphine–Ir Catalysts

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### Instrumentation and Chemicals

Solution NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for <sup>1</sup>H NMR, 75.4 MHz for <sup>13</sup>C NMR. Chemical shift values for <sup>1</sup>H and <sup>13</sup>C are reference to Me<sub>4</sub>Si and the residual solvent resonances respectively. Chemical shifts are reported in δ ppm. High-resolution mass spectra were recorded on a Thermo Fisher Scientific Exactive, JEOL JMS-T100LP mass spectrometer or JEOL JMS-T100 GC mass spectrometer at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F<sub>254</sub>. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. GLC analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. Melting points were determined on a micro melting point apparatus (Yanaco: MP-500D) using micro cover glass.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. [Ir(OMe)(cod)]<sub>2</sub> was prepared according to the literature.<sup>1</sup> Silica-SMAP<sup>2</sup> and Silica-TRIP<sup>3</sup> were prepared with CARiACT Q-10<sup>®</sup> according to the reported procedure. CARiACT Q-10 (Catalyst grade, 75–150 μm) was purchased from Fuji Silysia Chemical Ltd. and dehydrated by heating at 150 °C for 10 h and stored in a glovebox before use. All solvents for catalytic reactions were

degassed via four freeze–pump–thaw cycles before use. Bis(pinacolato)diboron was purchased from AllyChem Co., Ltd., and recrystallized from pentane before use.

## Experimental Procedures

**Typical Procedure for the Borylation of 2-Ethylpyridine (1a) with Immobilized Ligands (Table 1, entry 1).** In a glove box, Silica-SMAP (0.070 mmol/g, 85.7 mg, 0.006 mmol, 2.0 mol%), bis(pinacolato)diboron (**2**) (76.2 mg, 0.30 mmol), and anhydrous, degassed TBME (1.0 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of  $[\text{Ir}(\text{OMe})(\text{cod})]_2$  (2.0 mg, 0.003 mmol, 1.0 mol%) in TBME (2.0 mL) and 2-ethylpyridine (**1a**) (96.4 mg, 0.90 mmol) were added successively. The tube was sealed with a screw cap and removed from the glovebox. The reaction mixture was stirred at 25 °C for 12 h, and filtered through a glass pipet equipped with a cotton filter. The solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yields of the products **3a** and **4a** were determined by  $^1\text{H}$  NMR (66% and 21% respectively). The crude material was then purified by Kugelrohr distillation, to give the corresponding product **3a** (45.2 mg, 0.19 mmol in 64% isolated yield).

**Typical Procedure for the Borylation of 2-Ethylpyridine (1a) with Soluble Ligands (Table 1, entry 4).** In a glove box, bis(pinacolato)diboron (**2**) (76.2 mg, 0.30 mmol) and anhydrous, degassed TBME (1.35 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of Ph-SMAP (1.3 mg, 0.006 mmol, 2.0 mol%) in TBME (0.65 mL), a solution of  $[\text{Ir}(\text{OMe})(\text{cod})]_2$  (2.0 mg, 0.0030 mmol, 1.0 mol%) in TBME (1.0 mL) and 2-ethylpyridine (**1a**) (96.4 mg, 0.90 mmol) were added successively. The tube was sealed with a screw cap and removed from the glovebox. The reaction mixture was stirred at 25 °C for 12 h. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product **3a** was determined by  $^1\text{H}$  NMR (0%).

**Typical Procedure for the Borylation of 2-Alkylpyridine Derivatives (Table 2, Entry 1).** In a glove box, Silica-SMAP (0.070 mmol/g, 85.7 mg, 0.0060 mmol, 2.0 mol%), bis(pinacolato)diboron (**2**) (76.2 mg, 0.30 mmol), and anhydrous, degassed hexane (1.0 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of  $[\text{Ir}(\text{OMe})(\text{cod})]_2$  (2.0 mg, 0.0030 mmol, 1.0 mol%) in hexane (2.0 mL) and 2-isopropylpyridine (**1b**) (109.0 mg, 0.9 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 60 °C for 12 h, and filtered through a glass pipet equipped with a cotton filter. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was

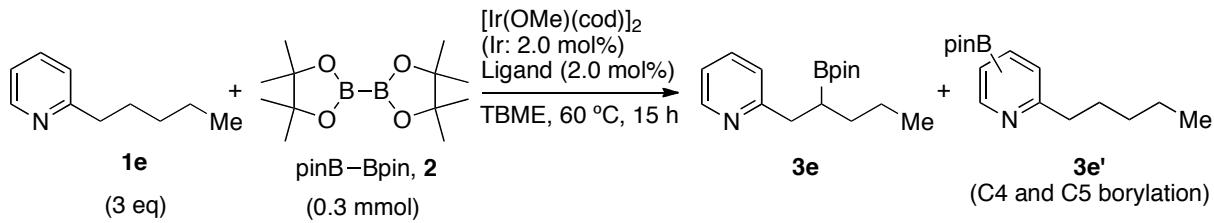
added to the residue. The yield of the product **3b** was determined by <sup>1</sup>H NMR (109%). The crude material was then purified by Kugelrohr distillation, to give the corresponding product **3b** (52.0 mg, 0.22 mmol in 73% isolated yield).

**Procedure for the One-Carbon Homologation Following Oxidation of **3f** (Scheme 2, Upper Side).** Under Ar atmosphere, **3f** (64.7 mg, 0.20 mmol), bromochloromethane (51.7 mg, 0.4 mmol), and anhydrous THF (2.0 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. The tube was sealed with a screw cap with a Teflon-coated silicon rubber septum. After the mixture was cooled to -78 °C, <sup>7</sup>BuLi in hexane (1.6 M, 24.4  $\mu$ L, 0.4 mmol) was added. The mixture was stirred at -78°C for 5 min, and stirred at room temperature for 30 min. After the reaction, solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue and the yield of desired product 2-[2-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]-pyridine (**5**) was determined by <sup>1</sup>H NMR (56%) in the crude mixture. The resulting product **5** was used to next reaction without further purification. The boronate **5**, THF (0.6 mL), water (0.6 mL) and sodium perborate tetrahydrate (51.7 mg, 0.34 mmol) were placed in a round bottom flask, and the reaction mixture was stirred vigorously at room temperature for 2 h under air. After the reaction, solvent and water were evaporated under reduced pressure. The concentrate was suspended in CHCl<sub>3</sub>, filtered through a pipet equipped with cotton. The filtrate was concentrated under reduced pressure, and the crude mixture was then purified by silica gel chromatography to give the corresponding alcohol **6** (24.5 mg, 0.11 mmol in 54% isolated yield in two steps).

**Procedure for the Oxidation of **3h** (Scheme 2, Bottom Side).** The oxidation of **3h** was performed according to the reported procedure.<sup>4</sup> THF (0.5 mL), water (0.5 mL), and sodium perborate tetrahydrate (46.1 mg, 0.3 mmol) were successively added to a vial tube containing **3h**. The reaction mixture was stirred vigorously at room temperature for 2 h under air. After the solvent and water were evaporated under reduced pressure, the mixture was suspended in CHCl<sub>3</sub>, and the suspension was filtered through a pipet equipped with cotton. The filtrate was concentrated under reduced pressure and the crude mixture was then purified by silica gel chromatography to give the corresponding alcohol **7** (13.1 mg, 0.74 mmol in 74% isolated yield). The trans stereo-configuration was determined by comparing the <sup>1</sup>H NMR spectrum of **3h** with that of the reported compound.<sup>5</sup>

## Ligand Effect

**Table S1.** Ligand Screening for Ir-Catalyzed Borylation of 2-Pentylpyridine (**1e**).<sup>a</sup>



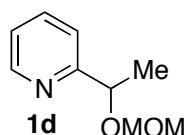
entry	ligand	NMR yield (%) <sup>b</sup>	
		$\mathbf{3e}$	$\mathbf{3e'}$
1	Silica-SMAP	106 (79)	11
2	Silica-TRIP	89	11
3	Ph-SMAP	0	0
4	PM <sub>3</sub>	0	0
5	PCy <sub>3</sub>	6	5
6	P'Bu <sub>3</sub>	0	0
7	PPh <sub>3</sub>	0	0
8	XPhos	0	0
9	dtbpy	0	154 <sup>c</sup>
10	none	0	0

<sup>a</sup> Conditions: **1e** (0.9 mmol), **2** (0.3 mmol),  $[\text{Ir(OMe)(cod)}]_2$  (Ir: 0.0060 mmol), ligand (0.0060 mmol), TBME (3.0 mL), 60 °C, 15 h. <sup>b</sup> <sup>1</sup>H-NMR yield based on **2**. Isolated yield is shown in parentheses. <sup>c</sup> C4 borylation 97% and C5 borylation 47%.

## Compounds Characterization

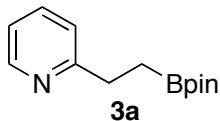
The substrates for borylation **1a**, **1e**, **1f** are known compounds. The substrates **1b**<sup>6</sup>, **1c**<sup>6</sup>, **1g**<sup>7</sup> and **1h**<sup>8</sup>, and alcohol **7**<sup>5</sup> are reported in the literatures.

**Preparation of 2-[1-(Methoxymethoxy)ethyl]pyridine (1d).** 2-[1-(Methoxymethoxy)ethyl]-pyridine (**1d**) was prepared via the protection of 2-[1-(hydroxy)ethyl]pyridine with methoxymethyl group.



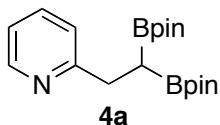
Colorless oil. **1H NMR** ( $\text{CDCl}_3$ )  $\delta$  1.53 (d,  $J = 6.6$  Hz, 3H), 3.38 (s, 3H), 4.63 (d,  $J = 6.6$  Hz, 1H), 4.72 (d,  $J = 6.6$  Hz, 1H), 4.86 (q,  $J = 6.6$  Hz, 1H), 7.19 (ddd,  $J = 7.8, 5.7, 0.9$  Hz, 1H), 7.43 (d,  $J = 7.8$  Hz, 1H), 7.70 (td,  $J = 7.8, 1.8$  Hz, 1H), 8.57 (dd,  $J = 5.7, 0.9$  Hz, 1H). **13C NMR** ( $\text{CDCl}_3$ )  $\delta$  22.00, 55.43, 75.46, 94.91, 120.27, 122.37, 136.75, 149.24, 162.93. **HRMS-ESI** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_9\text{H}_{13}\text{O}_2\text{NNa}$ , 190.08385; found, 190.08394.

## 2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (3a)



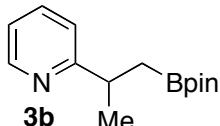
Colorless oil. **1H NMR** ( $\text{CDCl}_3$ )  $\delta$  1.08 (t,  $J = 7.8$  Hz, 2H), 1.25 (s, 12H), 2.99 (t,  $J = 7.8$  Hz, 2H), 7.18 (t,  $J = 6.3$  Hz, 1H), 7.25 (d,  $J = 7.8$  Hz, 1H), 7.67 (td,  $J = 7.8, 1.5$  Hz, 1H), 8.54 (d,  $J = 4.5$  Hz, 1H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ )  $\delta$  25.12 (4C), 31.74, 81.69 (2C), 121.42, 122.74, 137.75, 146.35, 163.73. A signal for the carbon directly attached to the boron atom was not observed. **HRMS-APCI** ( $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{21}\text{N}^{10}\text{BO}_2$ , 233.16964; found, 233.16962.

### 2-[2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (4a)



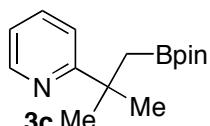
White solid. **M.p.** 75.6–77.3 °C. **1H NMR** ( $\text{CDCl}_3$ )  $\delta$  0.93 (t,  $J = 8.1$  Hz, 1H), 1.24 (s, 12H), 1.25 (s, 12H), 3.19 (d,  $J = 8.1$  Hz, 2H), 7.25 (m, 1H), 7.32 (d,  $J = 7.8$  Hz, 1H), 7.74 (td,  $J = 7.8, 1.8$  Hz, 1H), 8.56 (d,  $J = 5.4$  Hz, 1H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ )  $\delta$  25.30 (4C), 25.58 (4C), 33.58, 81.53 (4C), 121.83, 123.06, 139.07, 143.59, 164.00. A signal for the carbon directly attached to the boron atom was not observed. **HRMS-ESI** ( $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{32}\text{N}^{10}\text{B}_2\text{O}_4$ , 358.25846; found, 358.25870.

### 2-[1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-propan-2-yl]pyridine (3b)



Colorless oil. **1H NMR** ( $\text{CDCl}_3$ )  $\delta$  0.79 (dd,  $J = 14.1, 7.5$  Hz, 1H), 1.14 (dd,  $J = 14.1, 7.5$  Hz, 1H), 1.22 (s, 6H), 1.26 (s, 6H), 1.36 (d,  $J = 7.5$  Hz, 3H), 3.28 (sext,  $J = 7.5$  Hz, 1H), 7.27 (t,  $J = 6.3$  Hz, 1H), 7.38 (d,  $J = 7.5$  Hz, 1H), 7.79 (td,  $J = 7.5, 1.5$  Hz, 1H), 8.57 (d,  $J = 5.1$  Hz, 1H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ )  $\delta$  21.78, 25.39 (2C), 25.58 (2C), 37.02, 80.54 (2C), 121.52, 121.87, 139.19, 144.02, 167.68. A signal for the carbon directly attached to the boron atom was not observed. **HRMS-ESI** ( $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{23}\text{N}^{10}\text{BO}_2$ , 247.18527; found, 247.18544.

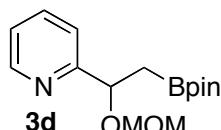
### 2-[2-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]pyridine (3c)



White solid. **M.p.** 72.5–74.0 °C. **1H NMR** ( $\text{CDCl}_3$ )  $\delta$  0.88 (s, 2H), 1.26 (s, 12H), 1.38 (s, 6H), 7.36 (ddd,  $J = 8.1, 5.7, 1.2$  Hz, 1H), 7.47 (d,  $J = 8.1$  Hz, 1H), 7.89 (td,  $J = 7.8, 1.2$  Hz, 1H), 8.58 (d,

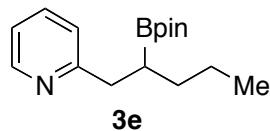
$J = 5.7$  Hz, 1H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  25.93 (4C), 31.07 (2C), 41.40, 79.32 (2C), 120.82, 122.56, 140.98, 141.59, 171.34. A signal for the carbon directly attached to the boron atom was not observed. **HRMS–ESI** ( $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{25}\text{BNO}_2$ , 261.20092; found, 261.20113.

**2-[1-(Methoxymethoxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (3d)**



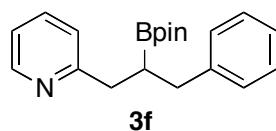
Colorless oil.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  1.16 (dd,  $J = 13.5, 9.0$  Hz, 1H), 1.21 (s, 6H), 1.25 (s, 6H), 1.53 (dd,  $J = 13.5, 6.9$  Hz, 1H), 3.41 (s, 3H), 4.71 (d,  $J = 6.6$  Hz, 1H), 4.86 (dd,  $J = 6.6$  Hz, 1H), 5.12 (dd,  $J = 9.0, 6.9$  Hz, 1H), 7.29 (t,  $J = 6.3$  Hz, 1H), 7.59 (d,  $J = 7.8$  Hz, 1H), 7.80 (td,  $J = 7.8, 1.5$  Hz, 1H), 8.57 (d,  $J = 5.1$  Hz, 1H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  25.01 (2C), 25.22 (2C), 55.50, 77.24, 81.53 (2C), 94.97, 121.44, 122.89, 138.50, 145.41, 162.79. A signal for the carbon directly attached to the boron atom was not observed. **HRMS–ESI** ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_4\text{N}^{10}\text{BNa}$ , 315.17269; found, 315.17269. Isolated product is contaminated with a trace of **1d**.

**2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyridine (3e)**



Colorless oil.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.1$  Hz, 3H), 1.12-1.18 (m, 2H), 1.23 (s, 6H), 1.24 (s, 6H), 1.29-1.40 (m, 2H), 1.42-1.55 (m, 1H), 2.82 (dd,  $J = 16.2, 6.6$  Hz, 1H), 3.07 (dd,  $J = 16.2, 6.6$  Hz, 1H), 7.22 (t,  $J = 5.7$  Hz, 1H), 7.28 (d,  $J = 7.4$  Hz, 1H), 7.71 (td,  $J = 7.4, 0.9$  Hz, 1H), 8.55 (d,  $J = 7.1$  Hz, 1H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  14.26, 22.24, 25.49 (2C), 25.60 (2C), 33.27, 38.09, 80.87 (2C), 121.66, 123.48, 138.44, 144.86, 162.72. A signal for the carbon directly attached to the boron atom was not observed. **HRMS–ESI** ( $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{27}\text{O}_2\text{N}^{10}\text{B}$ , 275.21657; found, 275.21659.

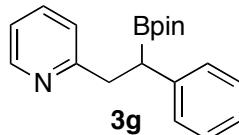
**2-[3-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]pyridine (3f)**



Colorless oil.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  1.28 (s, 12H), 1.48-1.56 (m, 1H), 2.29 (t,  $J = 14.4$  Hz, 1H), 2.74 (dd,  $J = 17.1, 5.7$  Hz, 1H), 2.97 (dd,  $J = 17.1, 7.1$  Hz, 1H), 3.06 (dd,  $J = 14.4, 4.5$  Hz, 1H), 7.15-7.29 (m, 6H), 7.34 (t,  $J = 6.3$  Hz, 1H), 7.80 (td,  $J = 7.8, 1.5$  Hz, 1H), 8.61 (d,  $J = 5.4$  Hz, 1H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  25.90 (2C), 26.13 (2C), 36.58, 36.75, 80.20 (2C), 122.29, 123.75, 125.27, 128.14 (2C), 128.85 (2C), 139.84, 143.07, 143.94, 162.55. A signal for the carbon directly attached

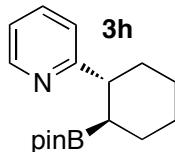
to the boron atom was not observed. **HRMS-ESI** (*m/z*): [M+H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>27</sub>N<sup>10</sup>BO<sub>2</sub>, 323.21657; found, 323.21662.

**2-[2-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (3g)**



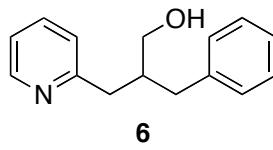
White solid. **M.p.** 114.2–116.1°C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>) δ 1.02 (s, 6H), 1.09 (s, 6H), 2.51 (t, *J* = 8.4 Hz, 1H), 3.40 (d, *J* = 8.4 Hz, 2H), 7.09 (m, 1H), 7.21–7.23 (m, 4H), 7.38–7.46 (m, 2H), 7.89 (td, *J* = 7.8, 1.5 Hz, 1H), 8.60 (d, *J* = 5.4 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>) δ 25.74 (2C), 26.37 (2C), 39.05, 80.13 (2C), 122.75, 123.44, 124.16, 127.69 (2C), 128.14 (2C), 140.42, 142.41, 145.83, 162.17. A signal for the carbon directly attached to the boron atom was not observed. **HRMS-ESI** (*m/z*): [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>25</sub>O<sub>2</sub>N<sup>10</sup>B, 309.20092; found, 309.20093.

**2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl]pyridine (3h)**



Colorless oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>) δ 0.97 (td, *J* = 12.0, 2.7, Hz, 1H), 1.11 (s, 6H), 1.17 (s, 6H), 1.21–1.61 (m, 4H), 1.77–1.90 (m, 3H), 2.17 (dd, *J* = 12.0, 3.3 Hz, 1H), 2.82 (td, *J* = 12.0, 3.3 Hz, 1H), 7.17 (tm, *J* = 6.6 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.69 (td, *J* = 7.8, 1.5 Hz, 1H), 8.52 (d, *J* = 4.5 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>) δ 24.99 (2C), 25.33 (2C), 26.46, 26.90, 27.42, 31.94, 46.43, 81.02 (2C), 120.89, 121.33, 137.81, 145.55, 165.67. A signal for the carbon directly attached to the boron atom was not observed. **HRMS-ESI** (*m/z*): [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>27</sub>N<sup>10</sup>BO<sub>2</sub>, 287.21657; found, 287.21664. The stereochemistry of **3h** was assigned by the coupling constant between the methine protons at C1 and C2 positions.

**2-Benzyl-3-(pyridin-2-yl)propan-1-ol (6)**



Colorless oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>) δ 2.34 (m, 1H), 2.59 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.72 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.93 (dd, *J* = 5.1, 3.0 Hz, 2H), 3.45 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.59 (dd, *J* = 11.1, 6.0 Hz, 1H), 7.11 (d, *J* = 7.8, 1H), 7.15–7.23 (m, 5H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.64 (td, *J* = 7.8, 1.5 Hz, 1H), 8.51 (d, *J* = 5.1 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>) δ 38.78, 39.51, 42.68, 64.45, 121.45, 124.25, 126.08, 128.43 (2C), 129.20 (2C) 137.23, 140.45, 148.37, 160.16. **HRMS-ESI** (*m/z*): [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>18</sub>NO, 228.138291; found, 228.13827.

## References

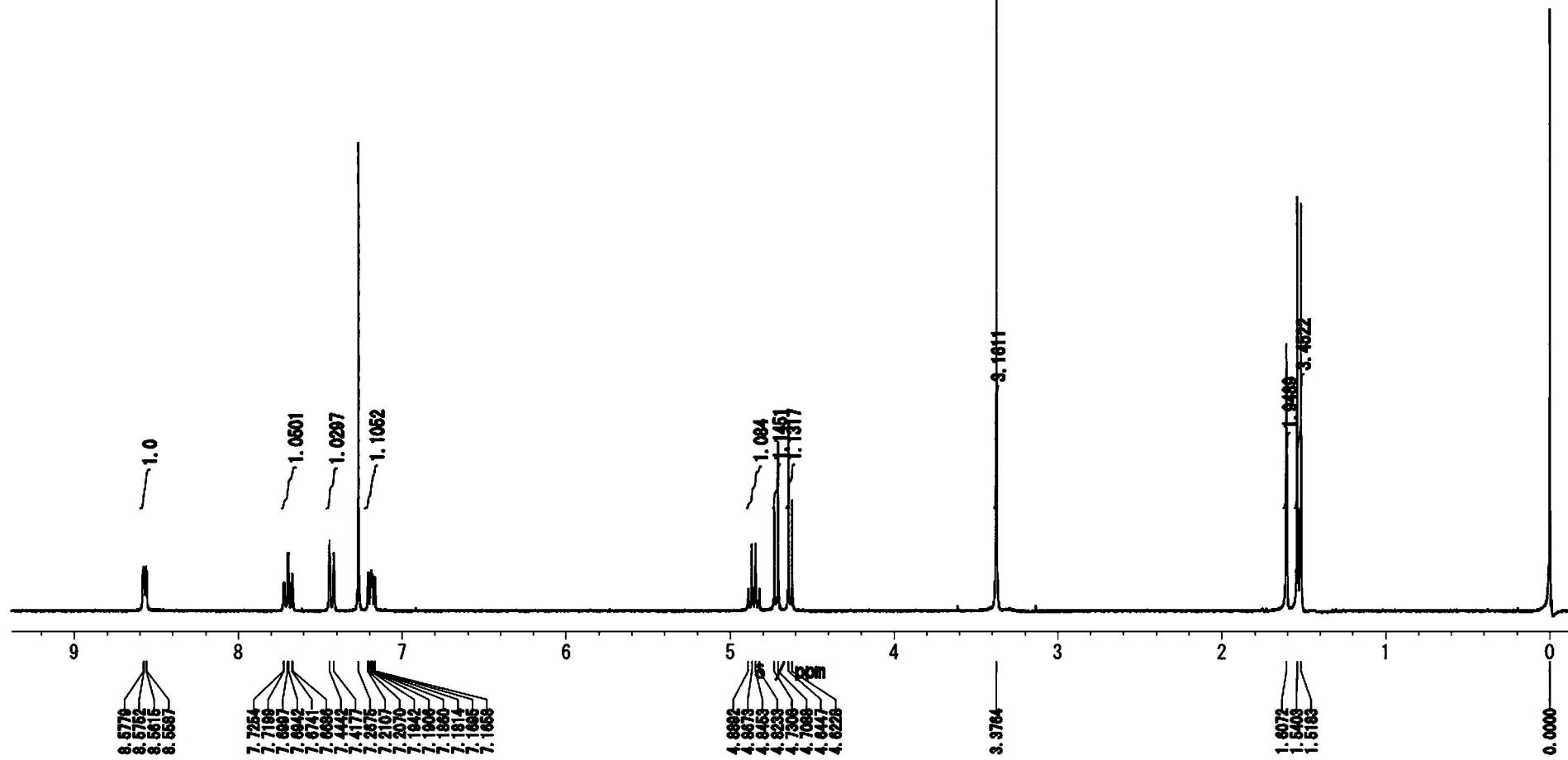
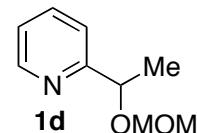
- (1) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.
- (2) (a) Hamasaki, G.; Ochida, A.; Hara, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 5381.  
(b) Hamasaki, G.; Kawamorita, S.; Ochida, A.; Akiyama, R.; Hara, K.; Fukuoka, A.; Asakura, K.; Chun, W. J.; Ohmiya, H.; Sawamura, M. *Organometallics* **2008**, *27*, 6495. (c) Kawamorita, S.; Ohmiya, H.; Hara, K.; Fukuoka, A.; Sawamura, M. *J. Am. Chem. Soc.* **2009**, *131*, 5058.
- (3) Kawamorita, S.; Miyazaki, T.; Ohmiya, H.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 19310.
- (4) Mun, S.; Lee, J.-E.; Yun, J. *Org. Lett.* **2006**, *8*, 4887.
- (5) Matsugi, M.; Itoh, K.; Nojima, M.; Hagimoto, Y.; Kita, Y. *Chem. Eur. J.* **2002**, *8*, 5551.
- (6) Pasquinet, E.; Rocca, P.; Marsais, F.; Godard, A.; QuEguiner, G. *Tetrahedron* **1998**, *54*, 8771.
- (7) Dieu, L. T.; Daugulis, O. *Org. Lett.* **2010**, *12*, 4277.
- (8) Lautens, M.; Roy, A.; Fukuoka, K.; Fagnou, K.; Martin-Matute, B. *J. Am. Chem. Soc.* **2001**, *123*, 5358.

Date Oct 16 12

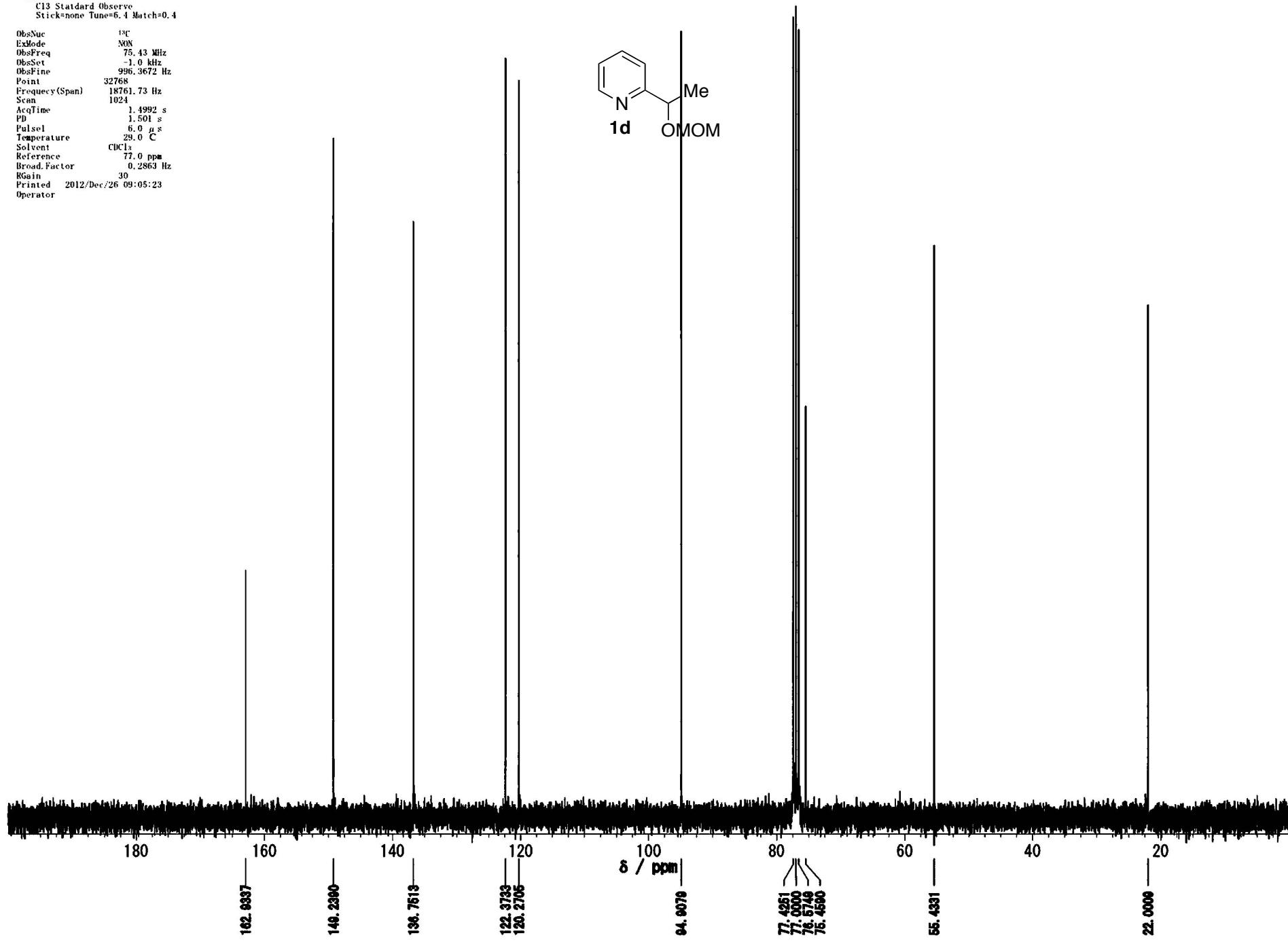
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Frequency(Span) 18761.73 Hz  
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PulseI 6.0  $\mu$ s  
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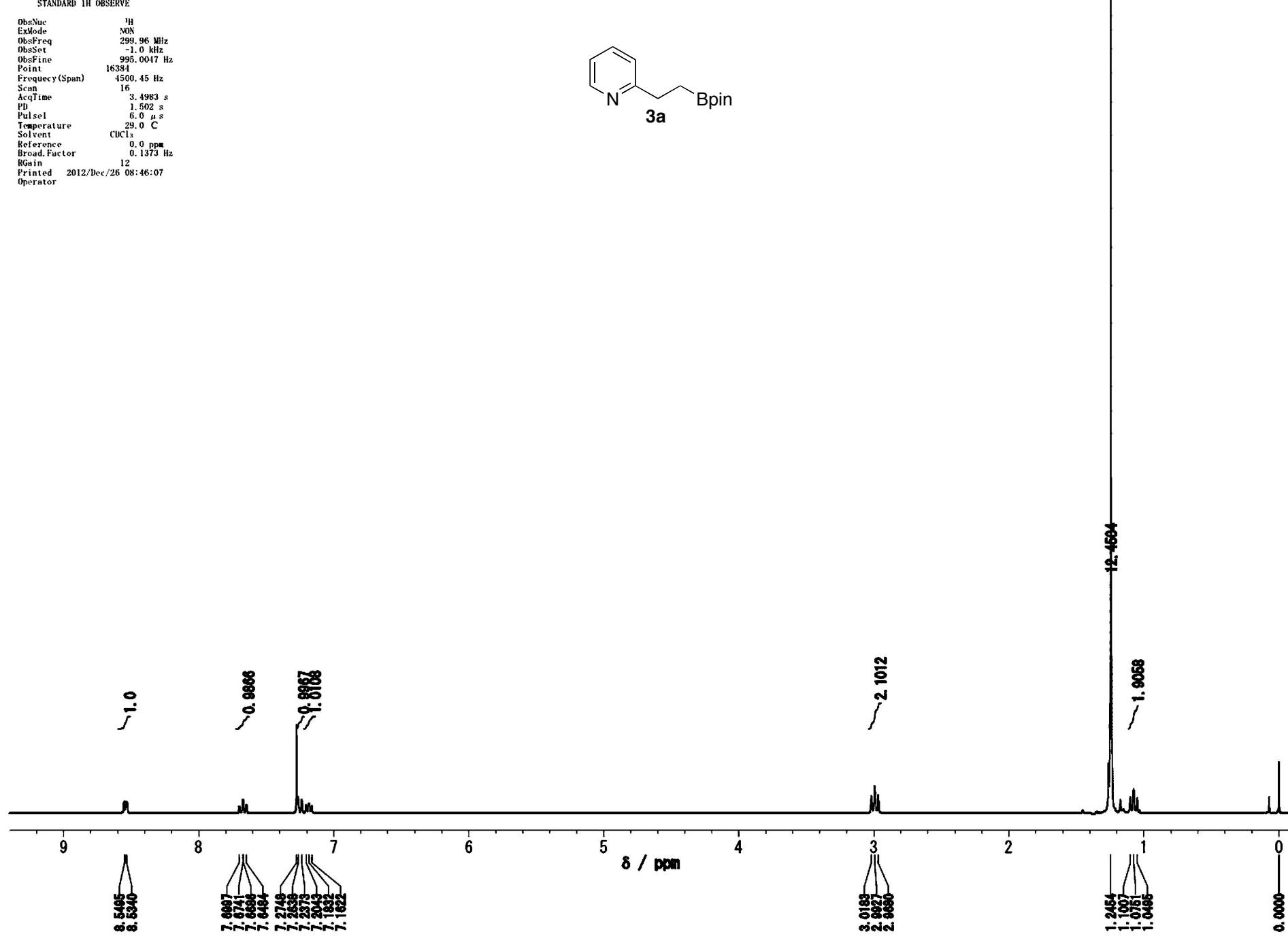
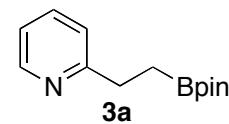


Date Oct 3 12

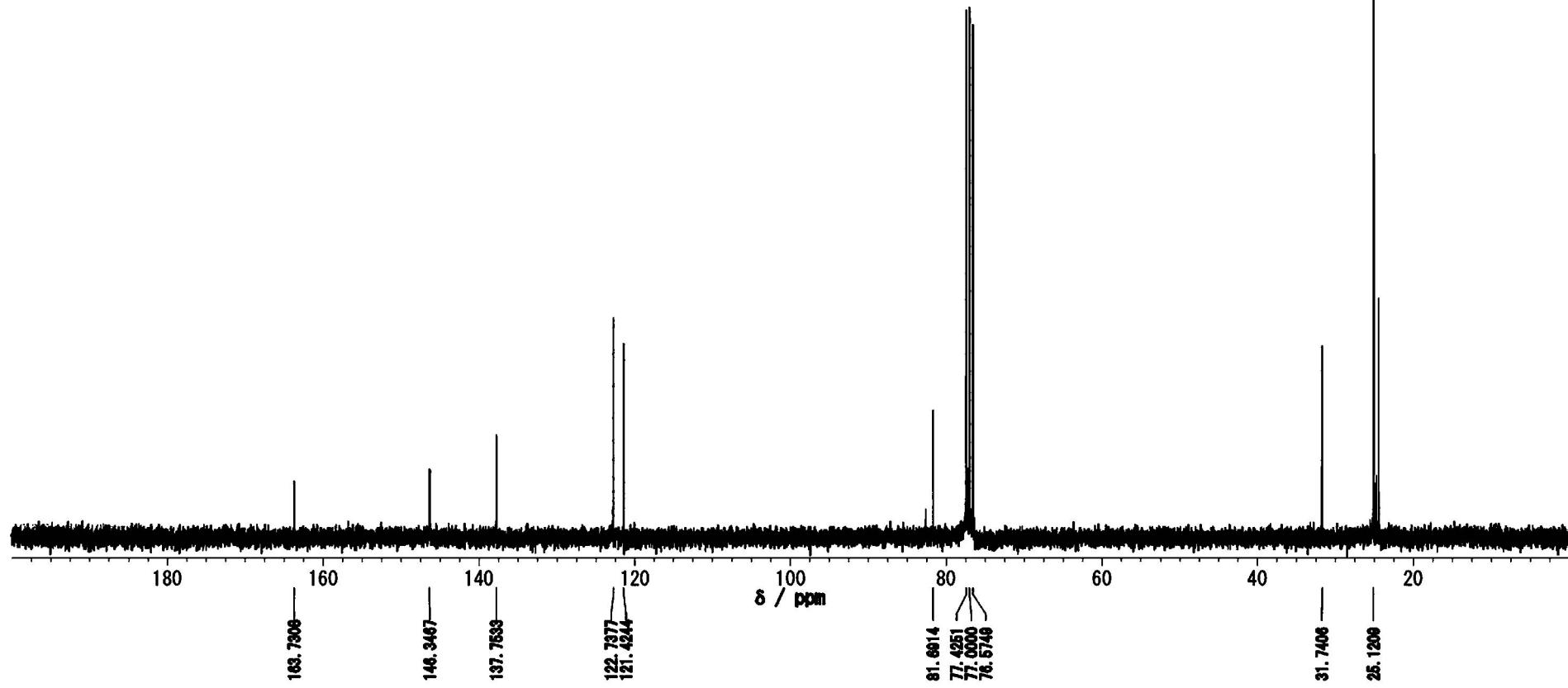
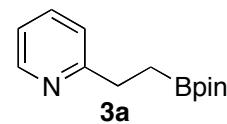
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Operator



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Date Oct 3 12

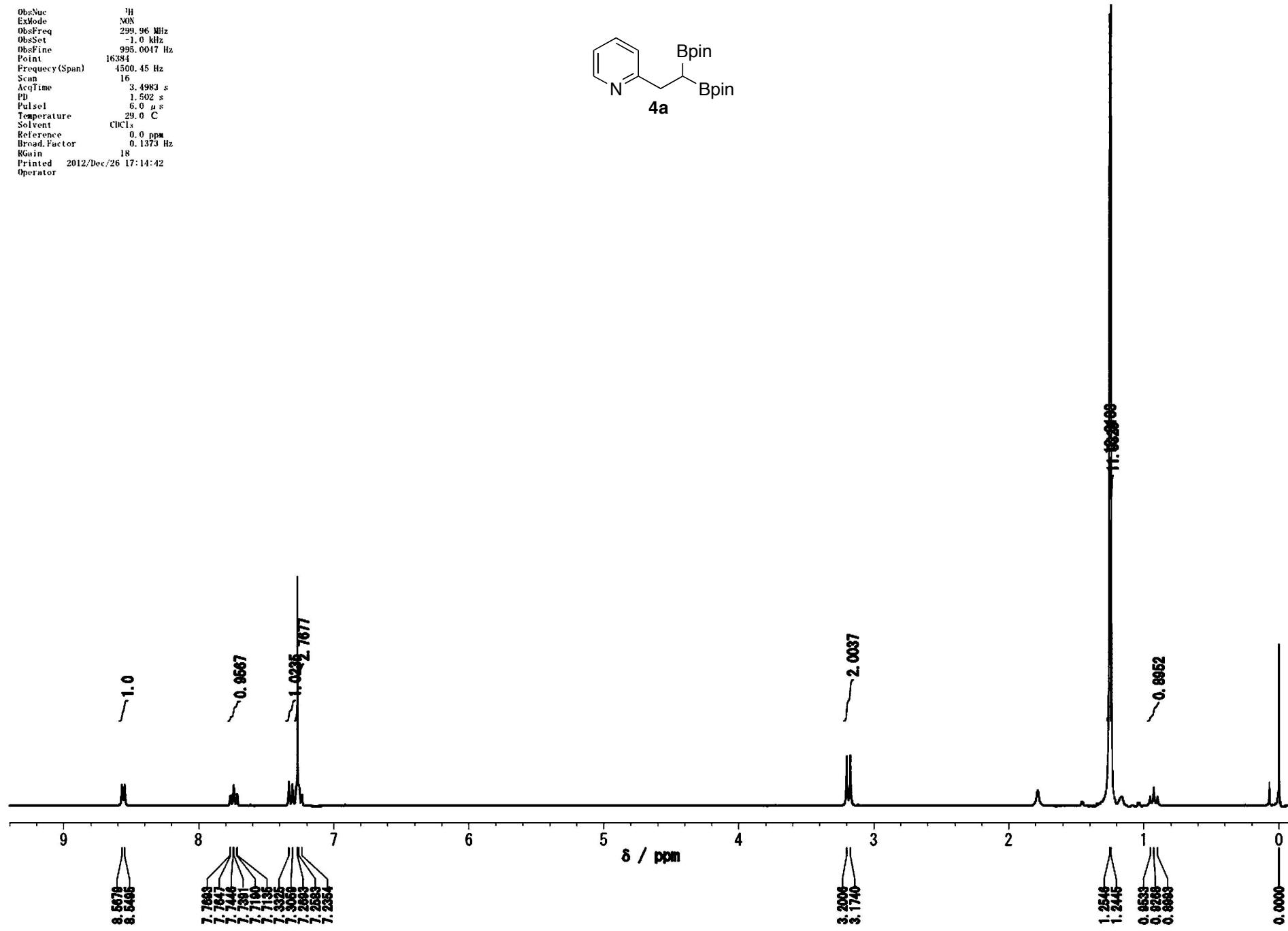
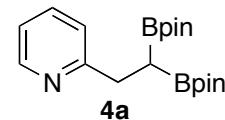
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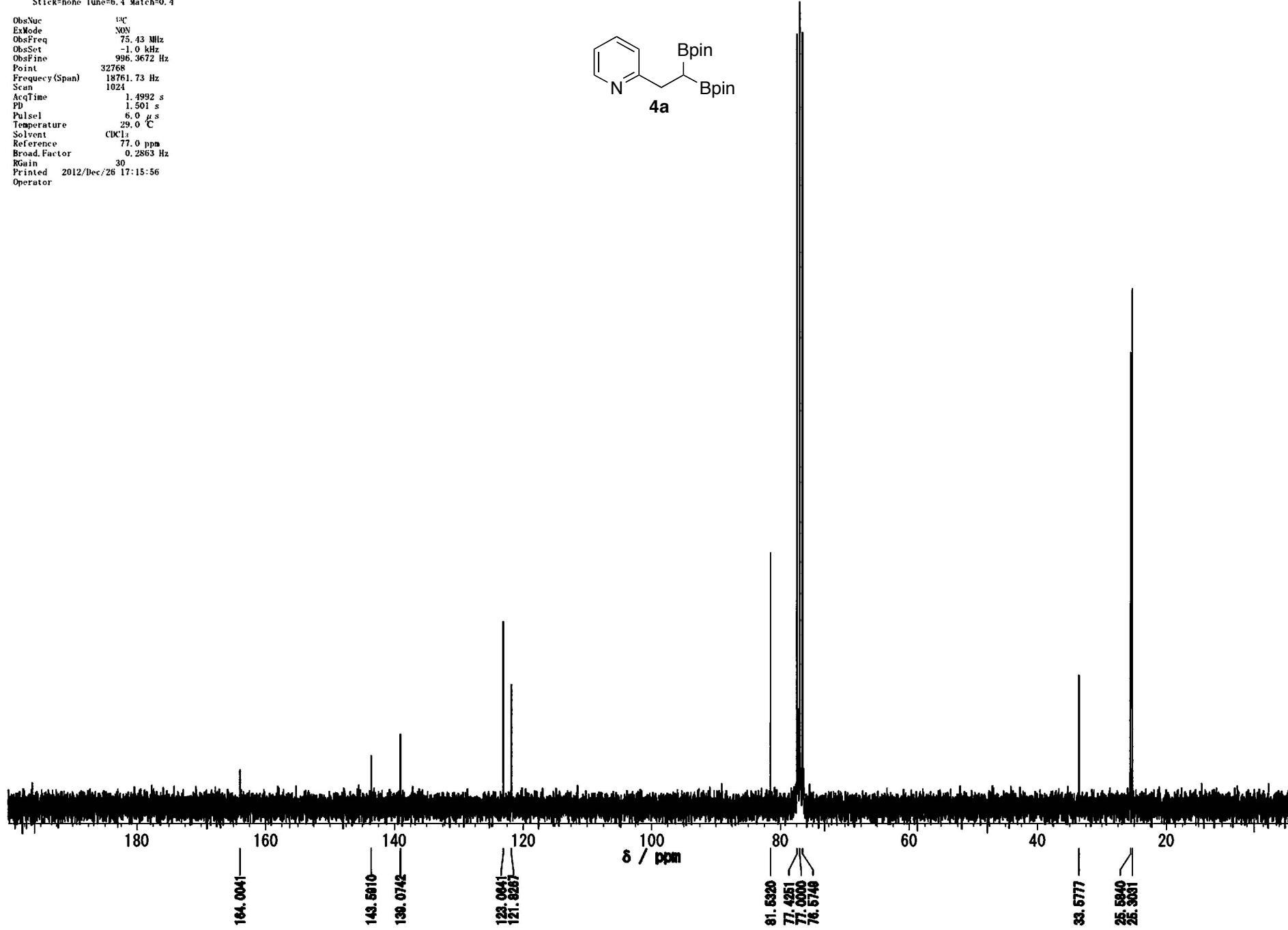
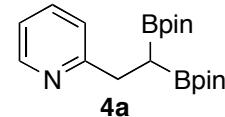
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Operator

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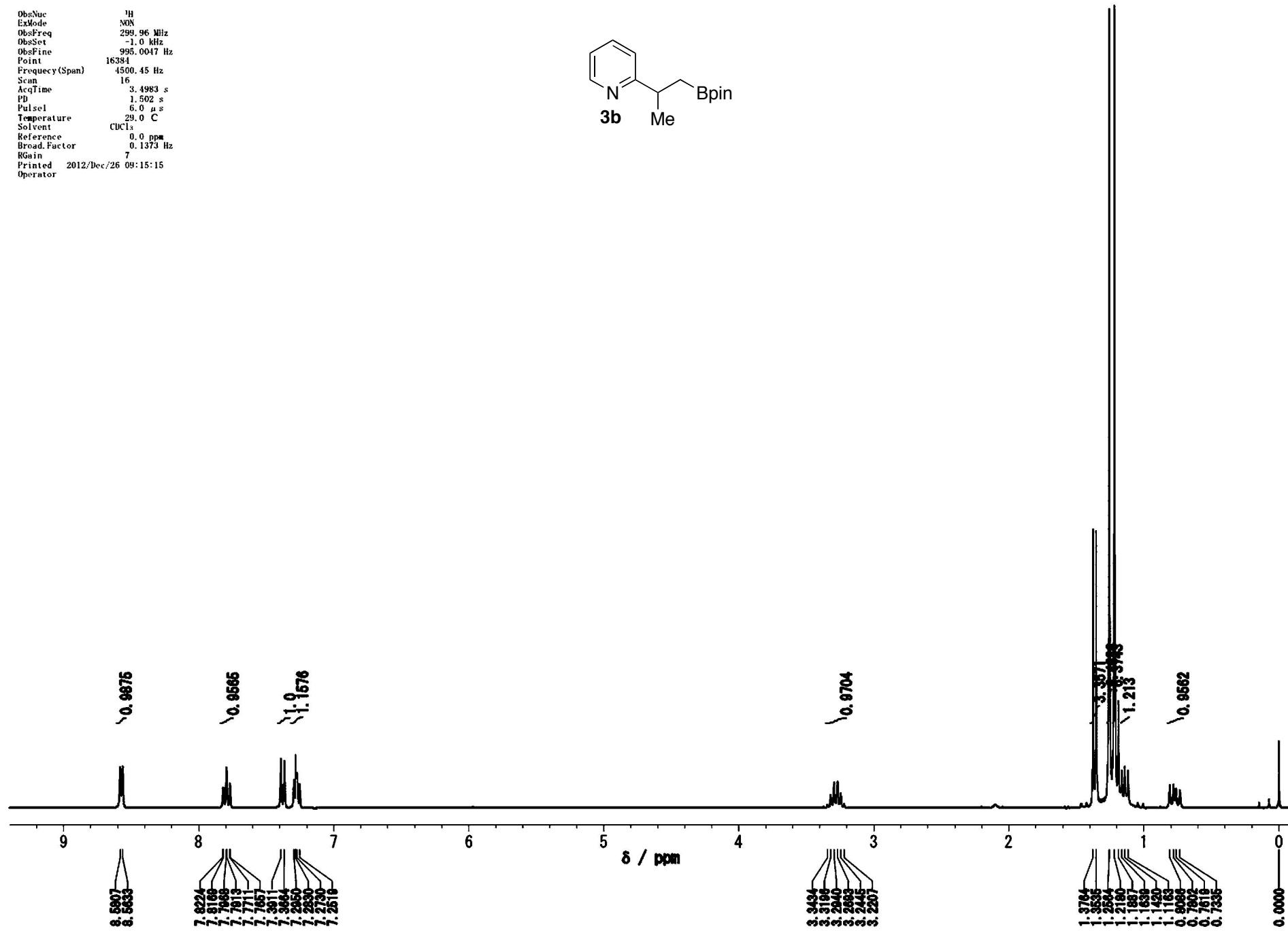
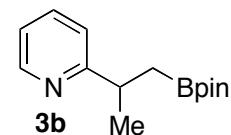


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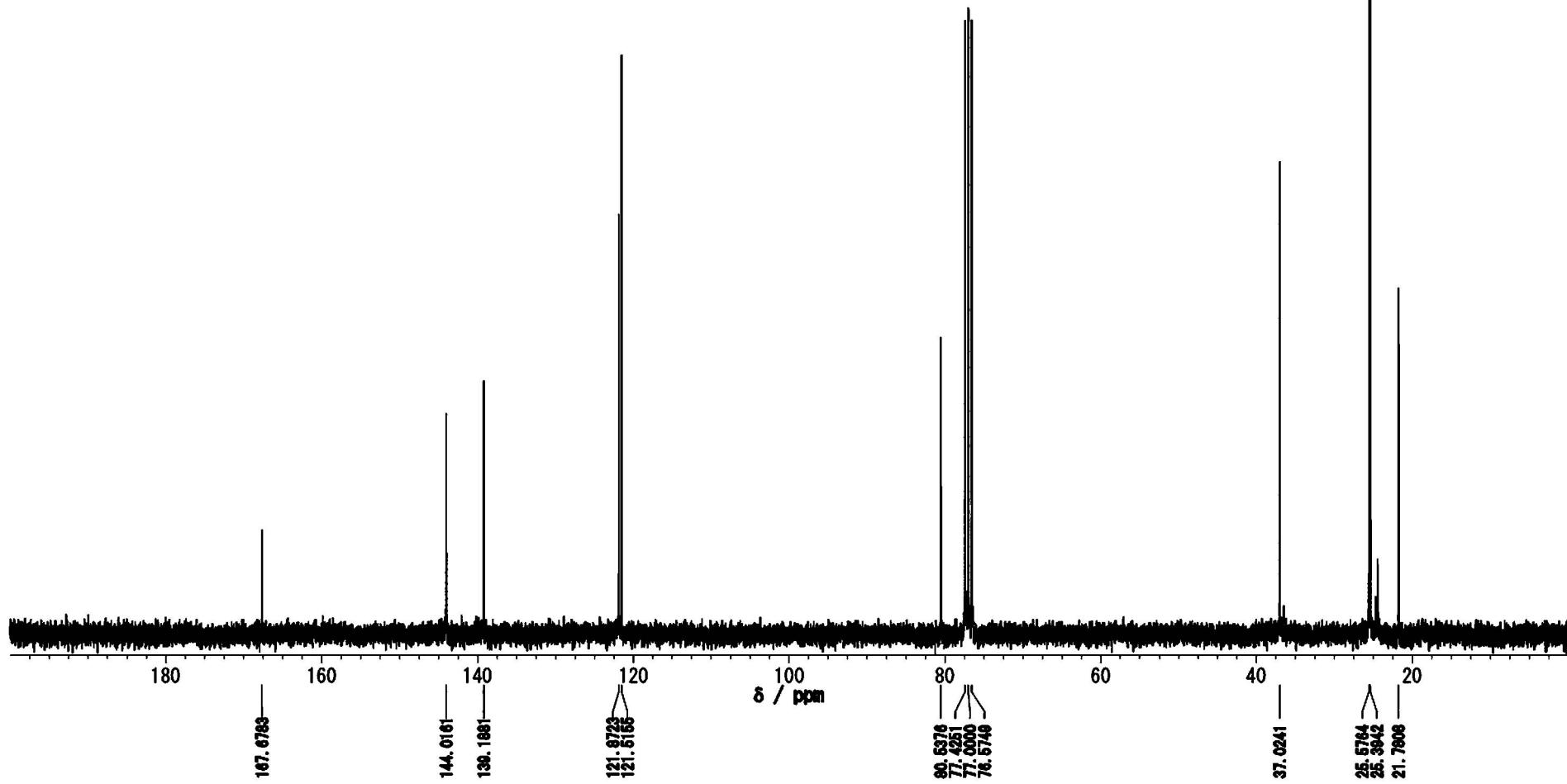
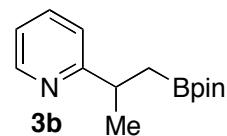
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Operator

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Frequency(Span) 18761.73 Hz  
Scan 1024  
AcqTime 1.4992 s  
PD 1.501 s  
Pulse 6.0  $\mu$ s  
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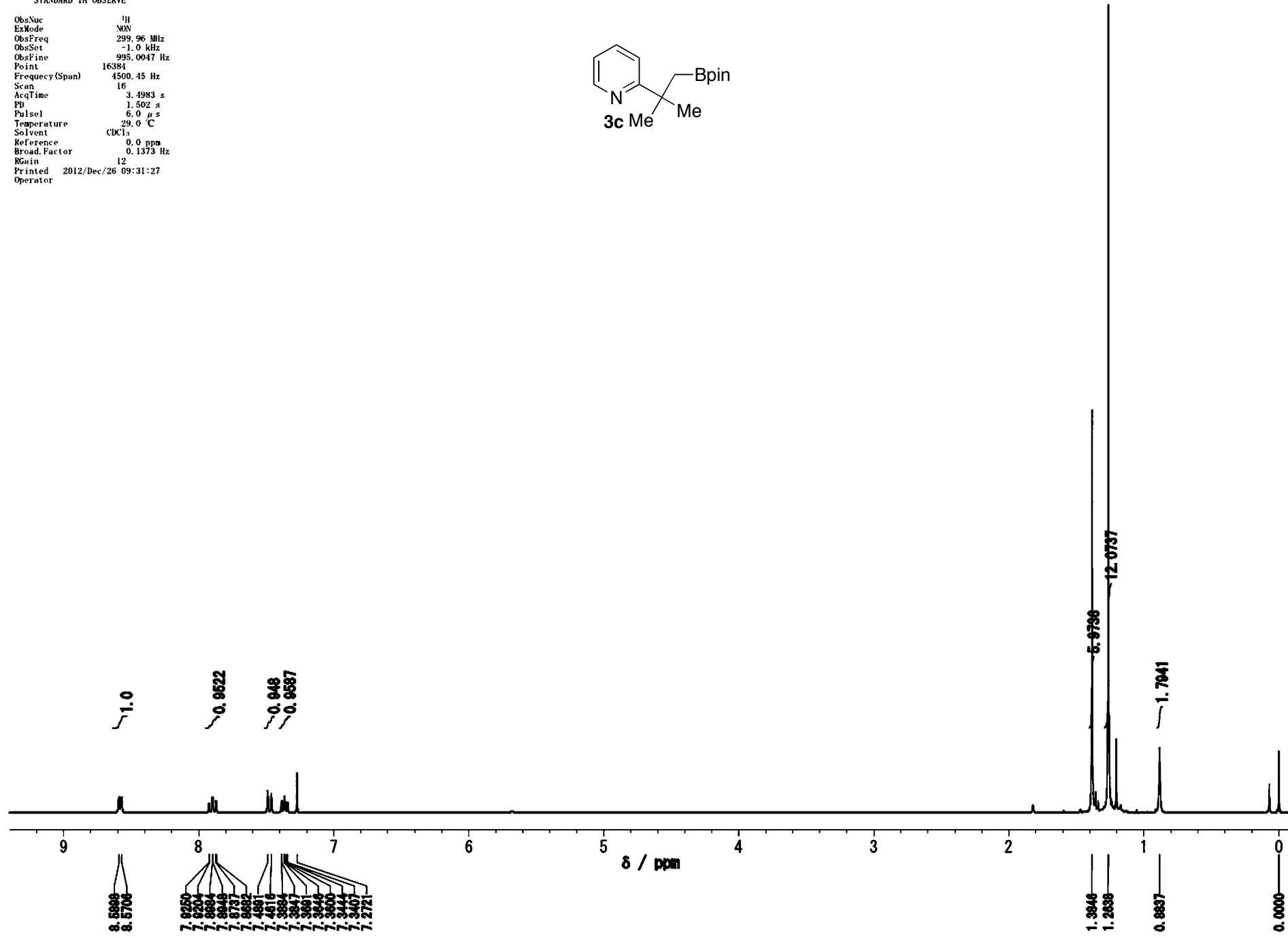
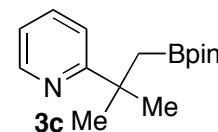


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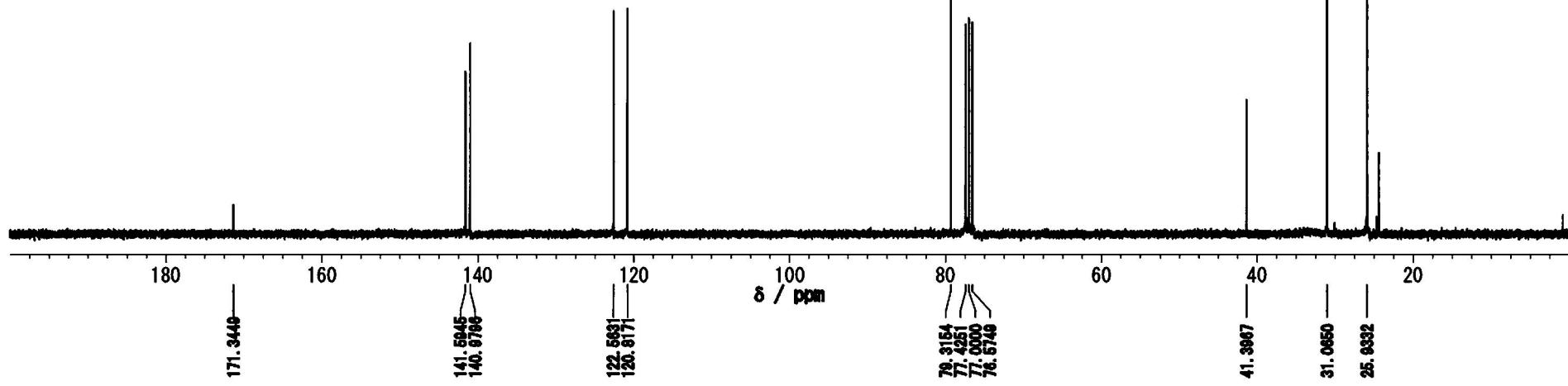
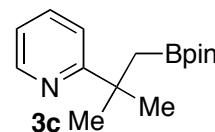
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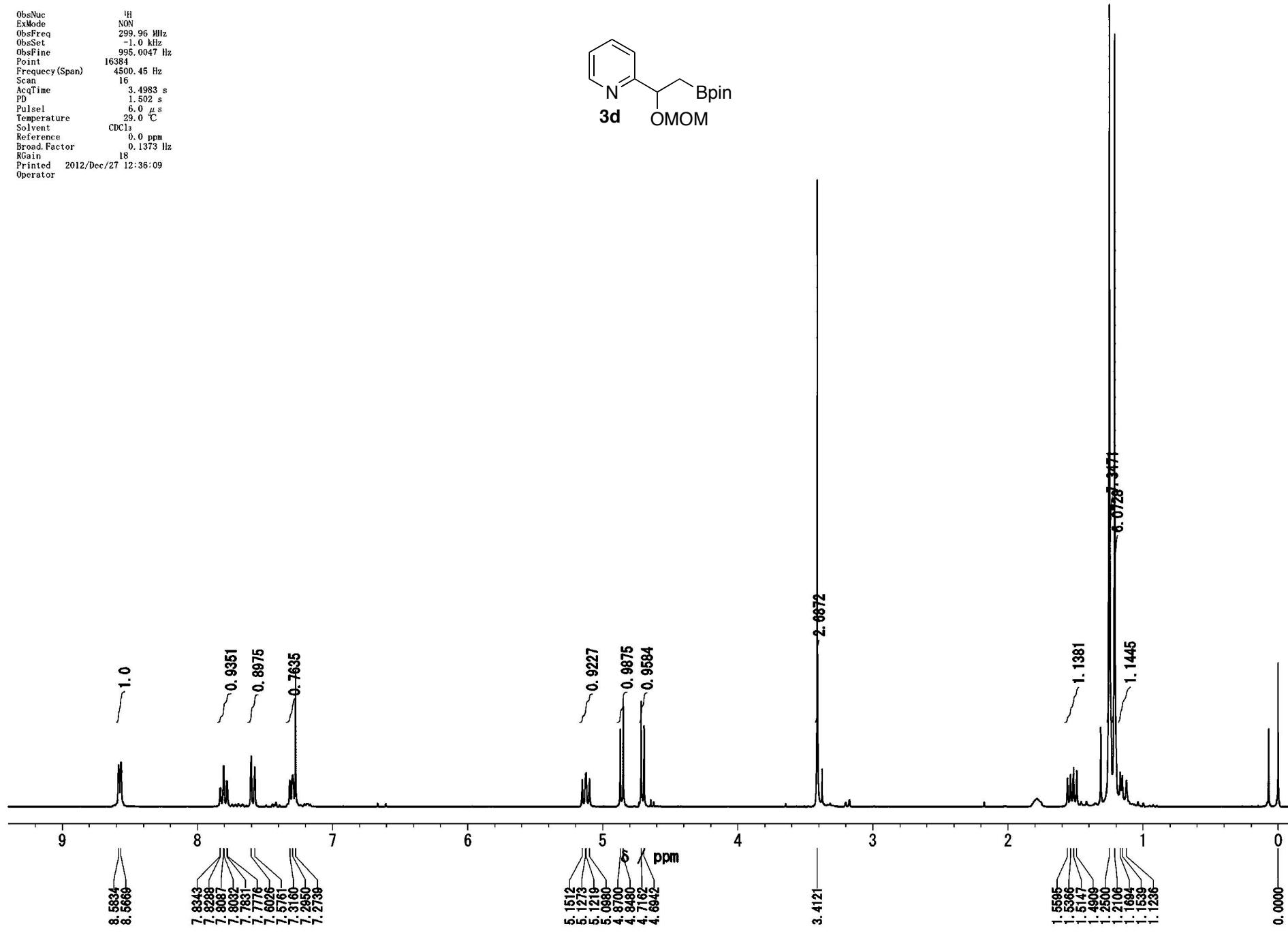
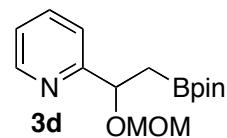


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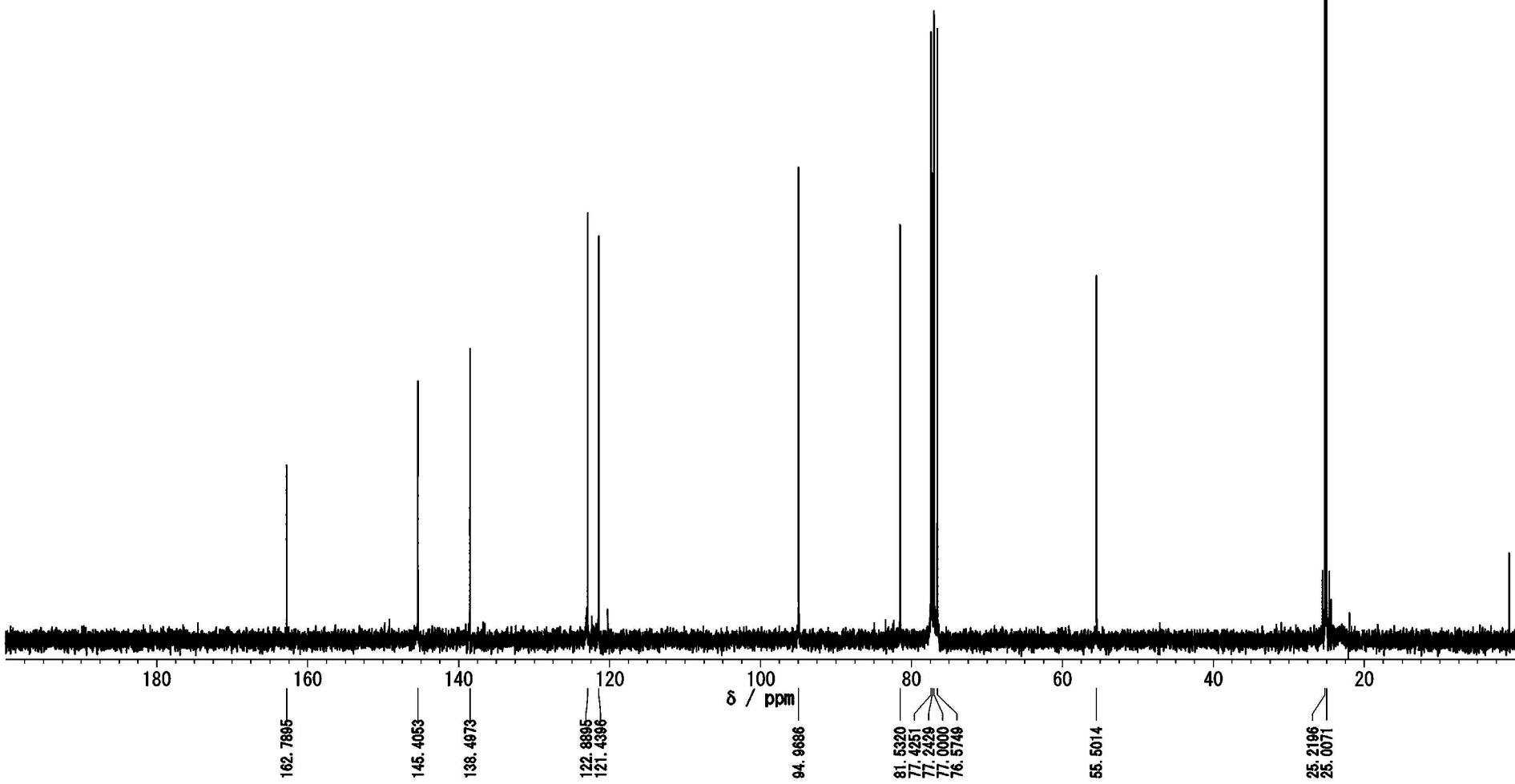
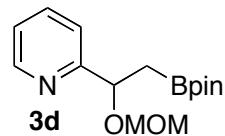
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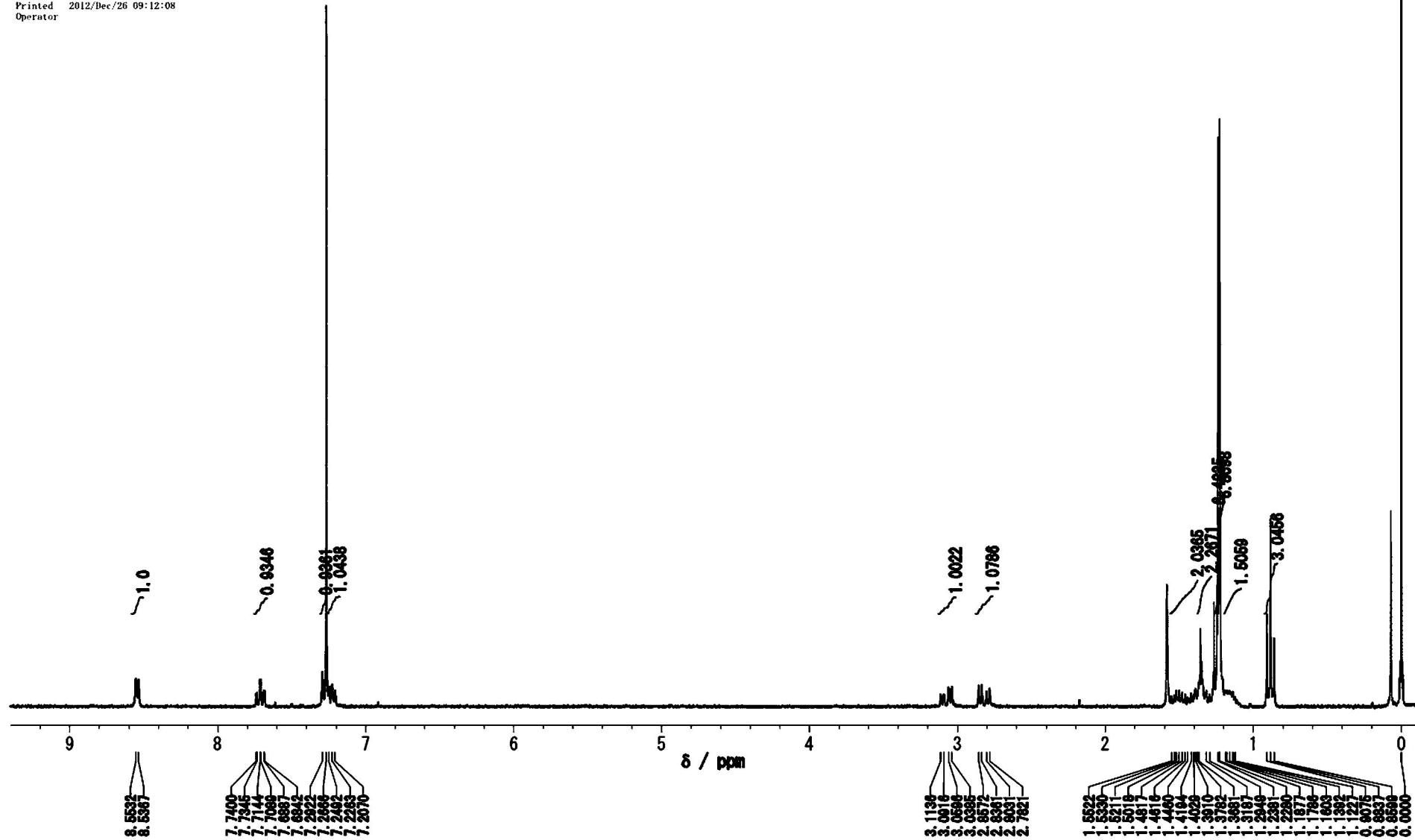
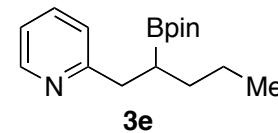


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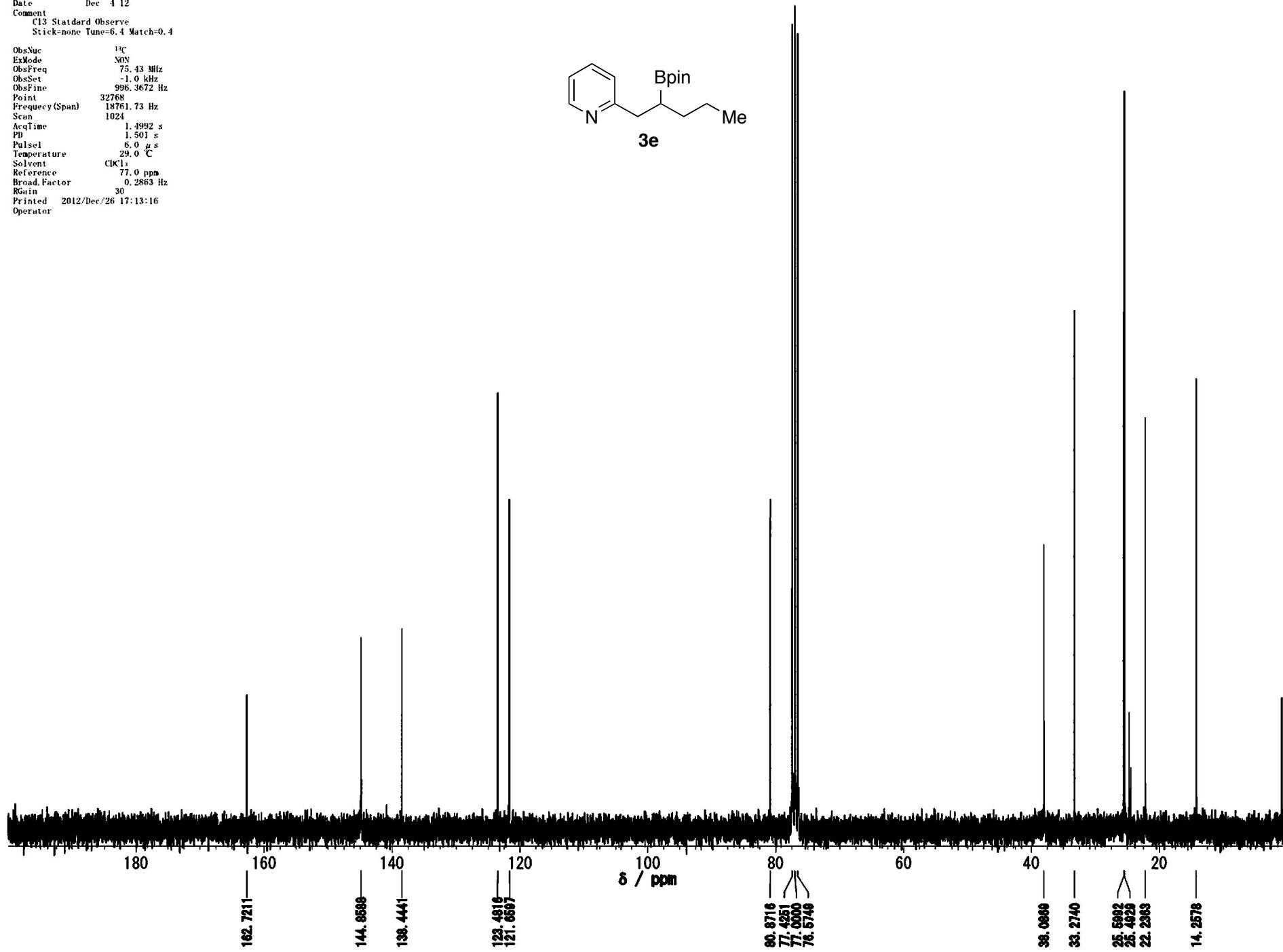
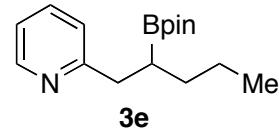
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Date Dec 4 12

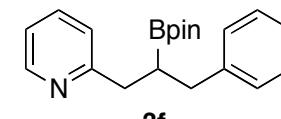
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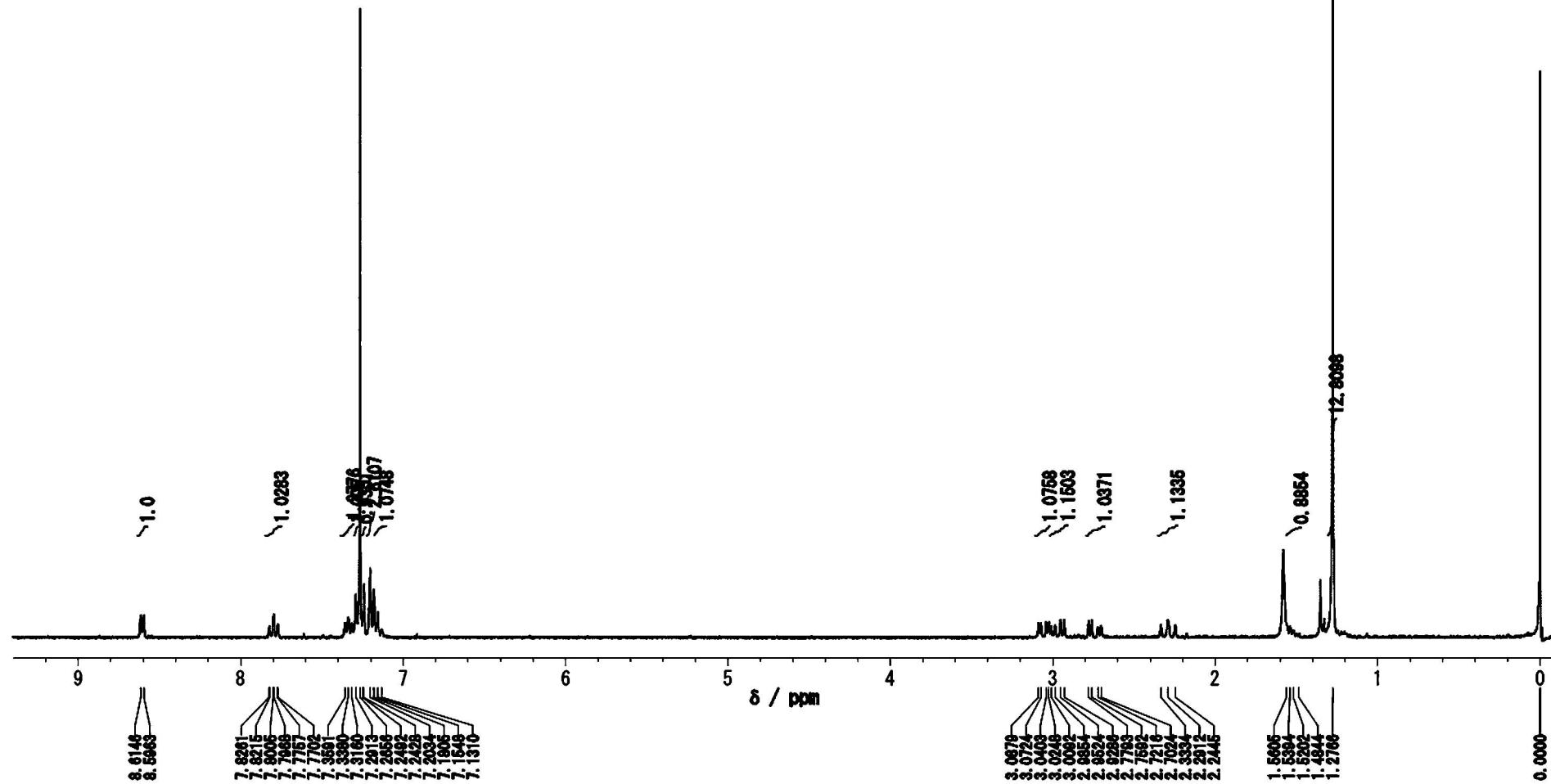
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Operator

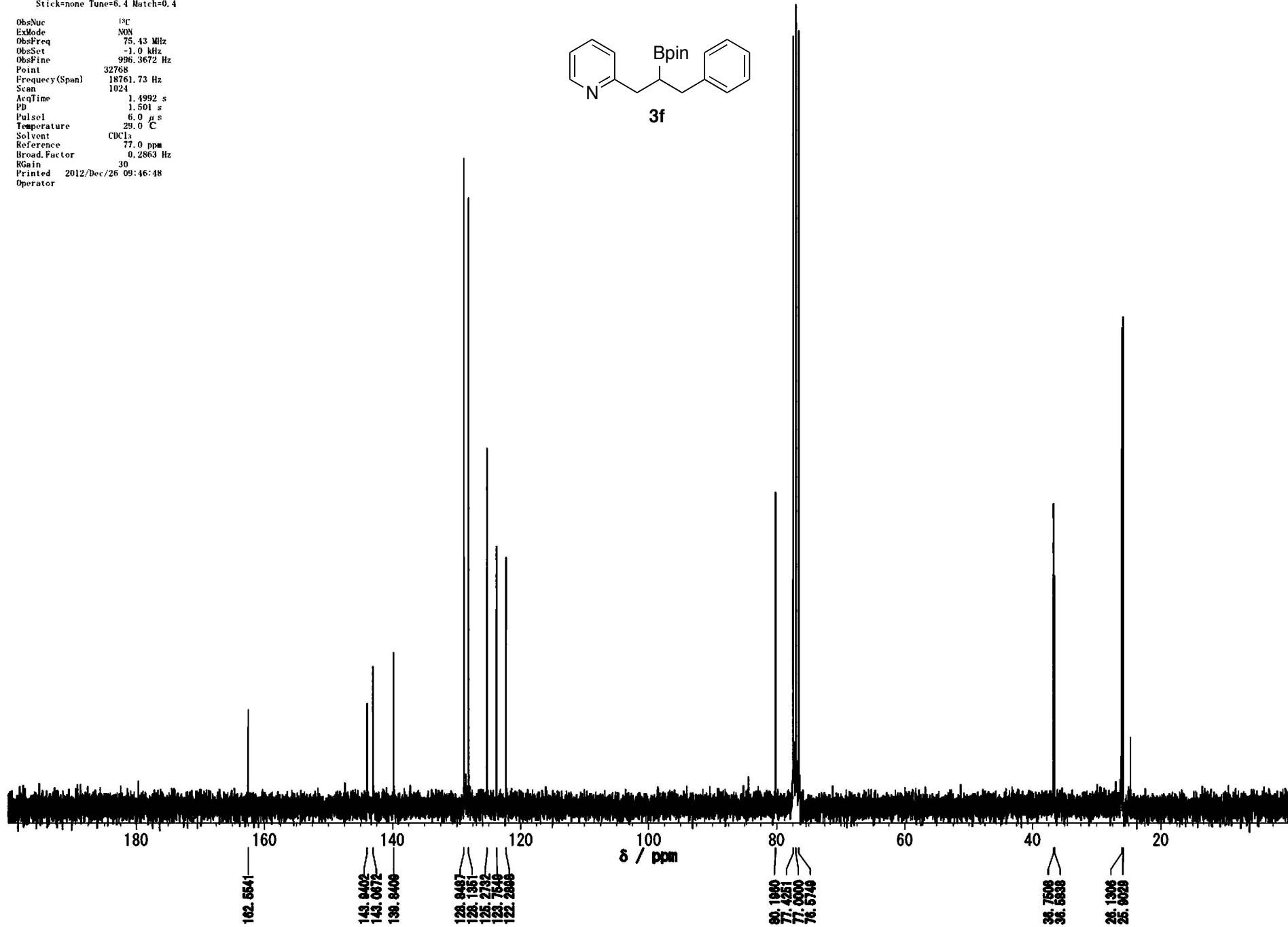
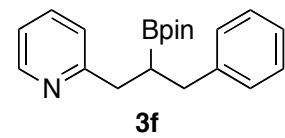
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3



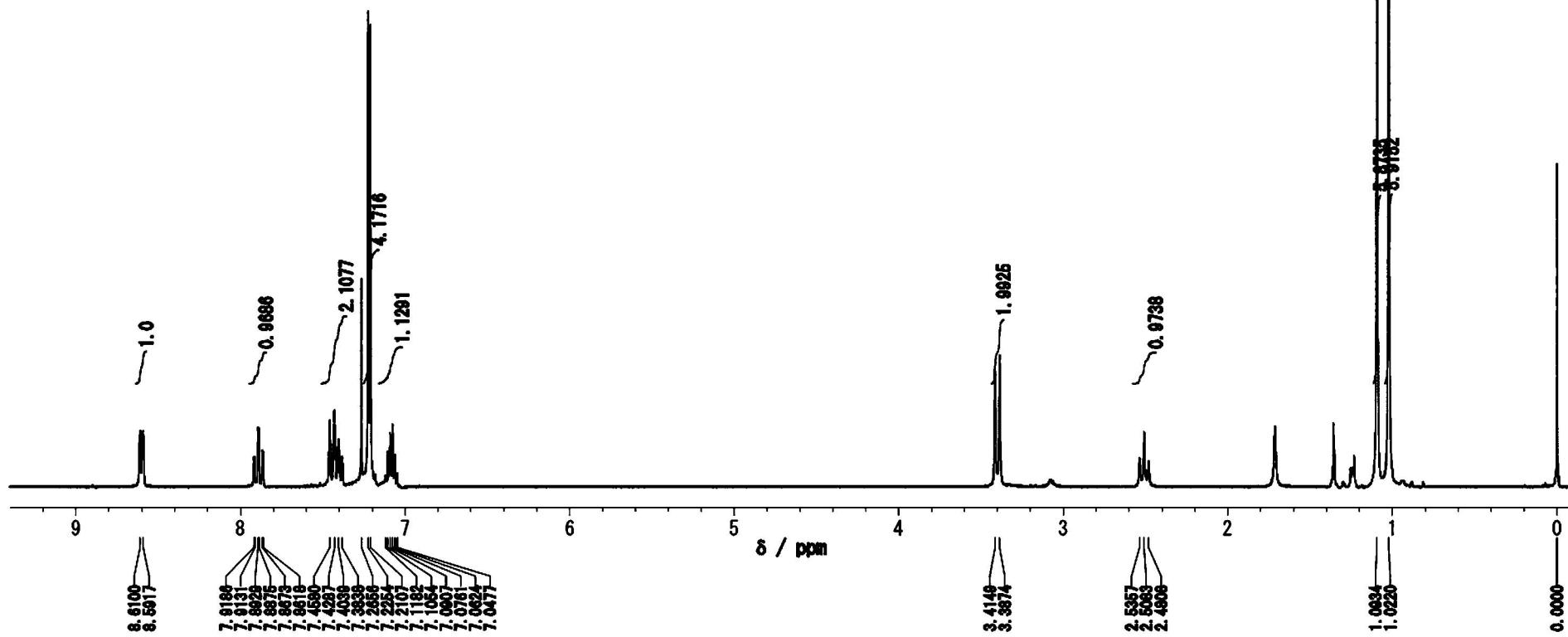
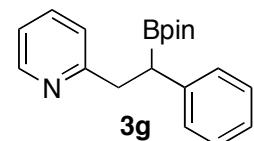
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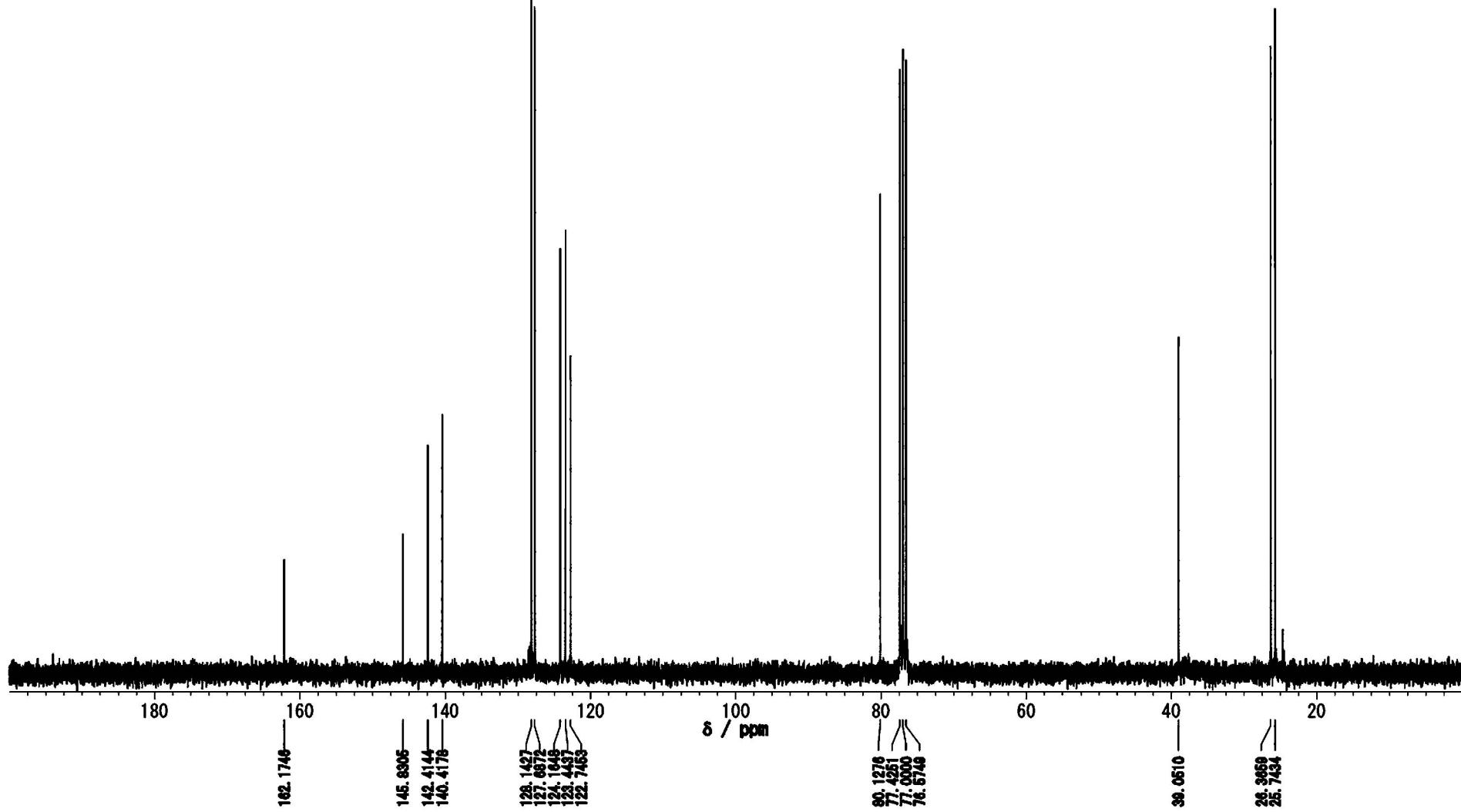
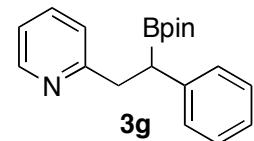
Date Oct 4 12

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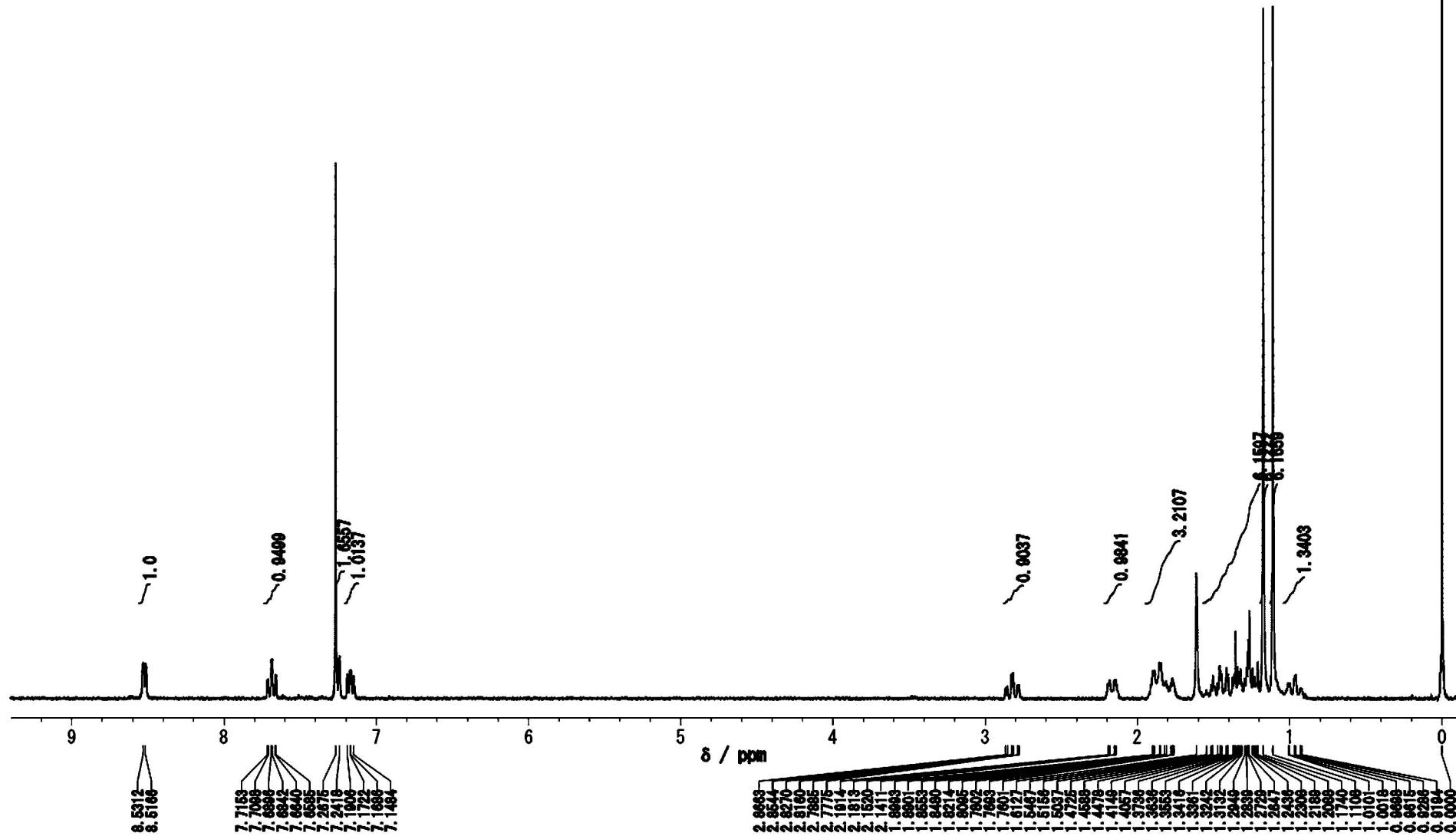
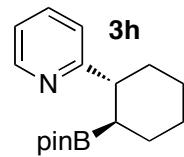
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Scan 1024  
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PD 1.501 s  
Pulse 6.0  $\mu\text{s}$   
Temperature 29.0  $^{\circ}\text{C}$   
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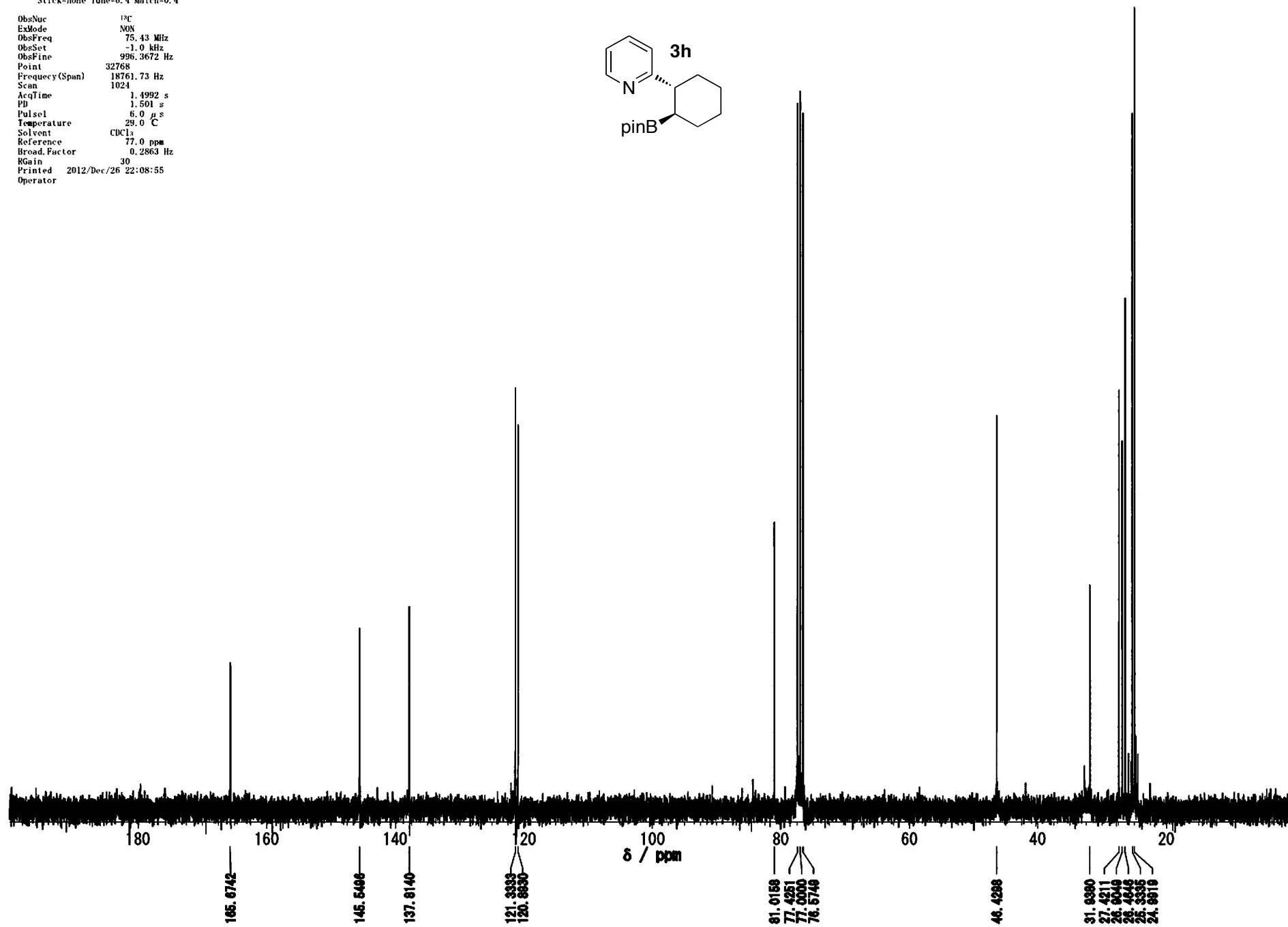
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Temperature 29.0 °C
Solvent CDCl3
Reference 0.0 ppm
Broad. Factor 0.1373 lb
RGain 30
Printed 2012/Dec/26 09:43:06
Operator

```



Date Nov 19 12  
 Comment  
 C13 Standard Observe  
 Stick=none Tune=6.4 Match=0.4  
 ObsNuc <sup>13</sup>C  
 ExMode NON  
 ObsFreq 75.43 MHz  
 ObsSet -1.0 kHz  
 ObsFine 996.3672 Hz  
 Point 32768  
 Frequency(Span) 18761.73 Hz  
 Scan 1024  
 AcqTime 1.4992 s  
 PD 1.501 s  
 Pulsol 6.0  $\mu$ s  
 Temperature 29.0 °C  
 Solvent CDCl<sub>3</sub>  
 Reference 77.0 ppm  
 Broad.Factor 0.2863 Hz  
 RGain 30  
 Printed 2012/Dec/26 22:08:55  
 Operator

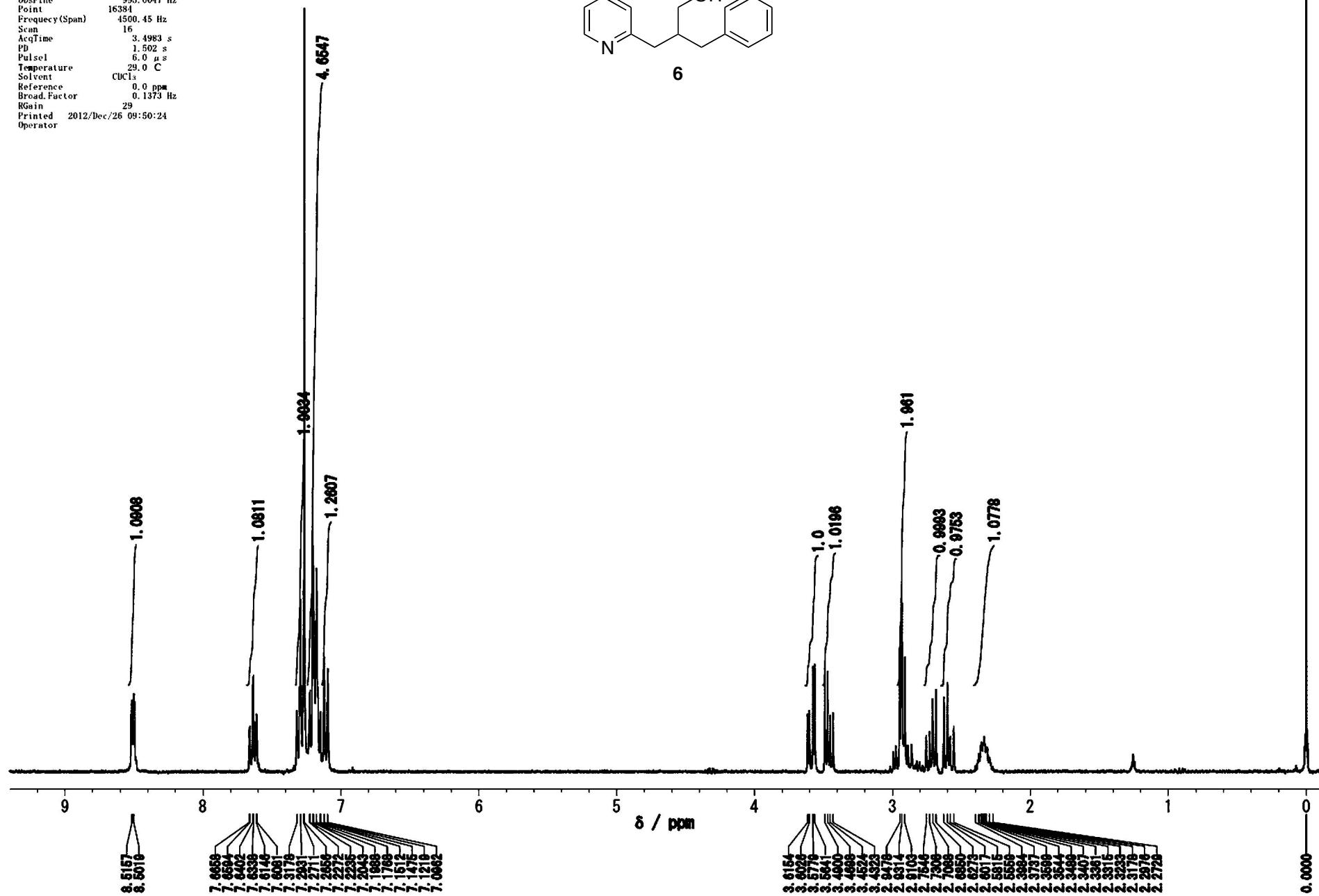
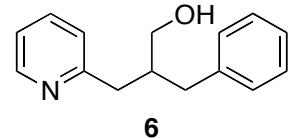


Date Dec 26 12

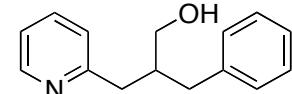
Comment

STANDARD 1H OBSERVE

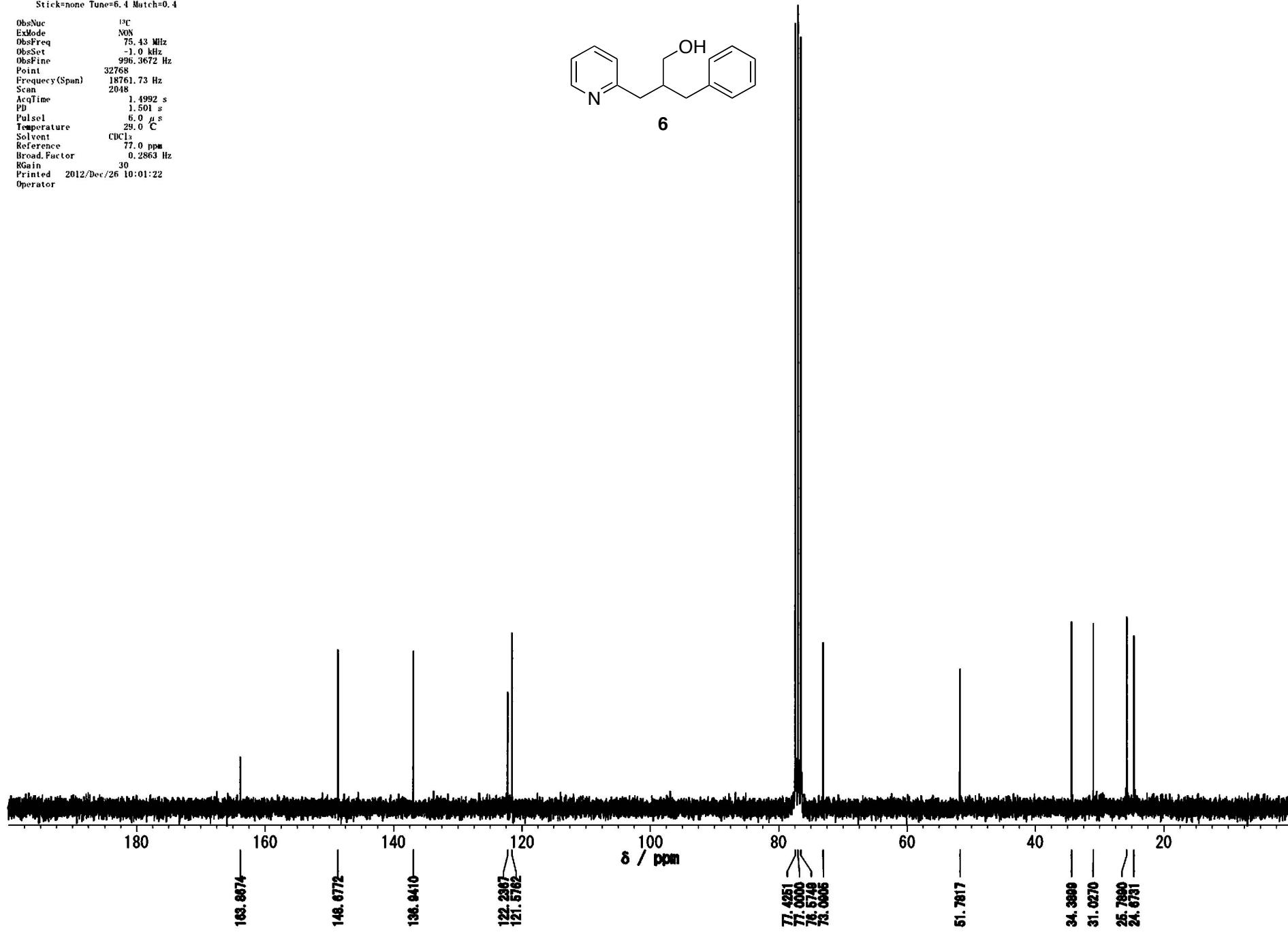
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ExMode NMR  
ObsFreq 299.96 MHz  
ObsSet -1.0 kHz  
ObsFine 995.0047 Hz  
Point 16384  
Frequency (Span) 4500.45 Hz  
Scan 16  
AcqTime 3.4983 s  
PD 1.502 s  
Pulse 6.0  $\mu\text{s}$   
Temperature 29.0  $^{\circ}\text{C}$   
Solvent  $\text{CDCl}_3$   
Reference 0.0 ppm  
Broad. Factor 0.1373 Hz  
RGain 29  
Printed 2012/Dec/26 09:50:24  
Operator



Date Dec 25 12  
Comment  
C13 Standard Observe  
Stick=none Tune=6.4 Match=0.4  
ObsNuc  $^{13}\text{C}$   
ExMode NON  
ObsFreq 75.43 MHz  
ObsSet -1.0 kHz  
ObsFine 996.3672 Hz  
Point 32768  
Frequency(Span) 18761.73 Hz  
Scan 2048  
AcqTime 1.4992 s  
PD 1.501 s  
Pulse 6.0  $\mu\text{s}$   
Temperature 29.0  $^{\circ}\text{C}$   
Solvent  $\text{CDCl}_3$   
Reference 77.0 ppm  
Broad.Factor 0.2863 Hz  
RGain 30  
Printed 2012/Dec/26 10:01:22  
Operator



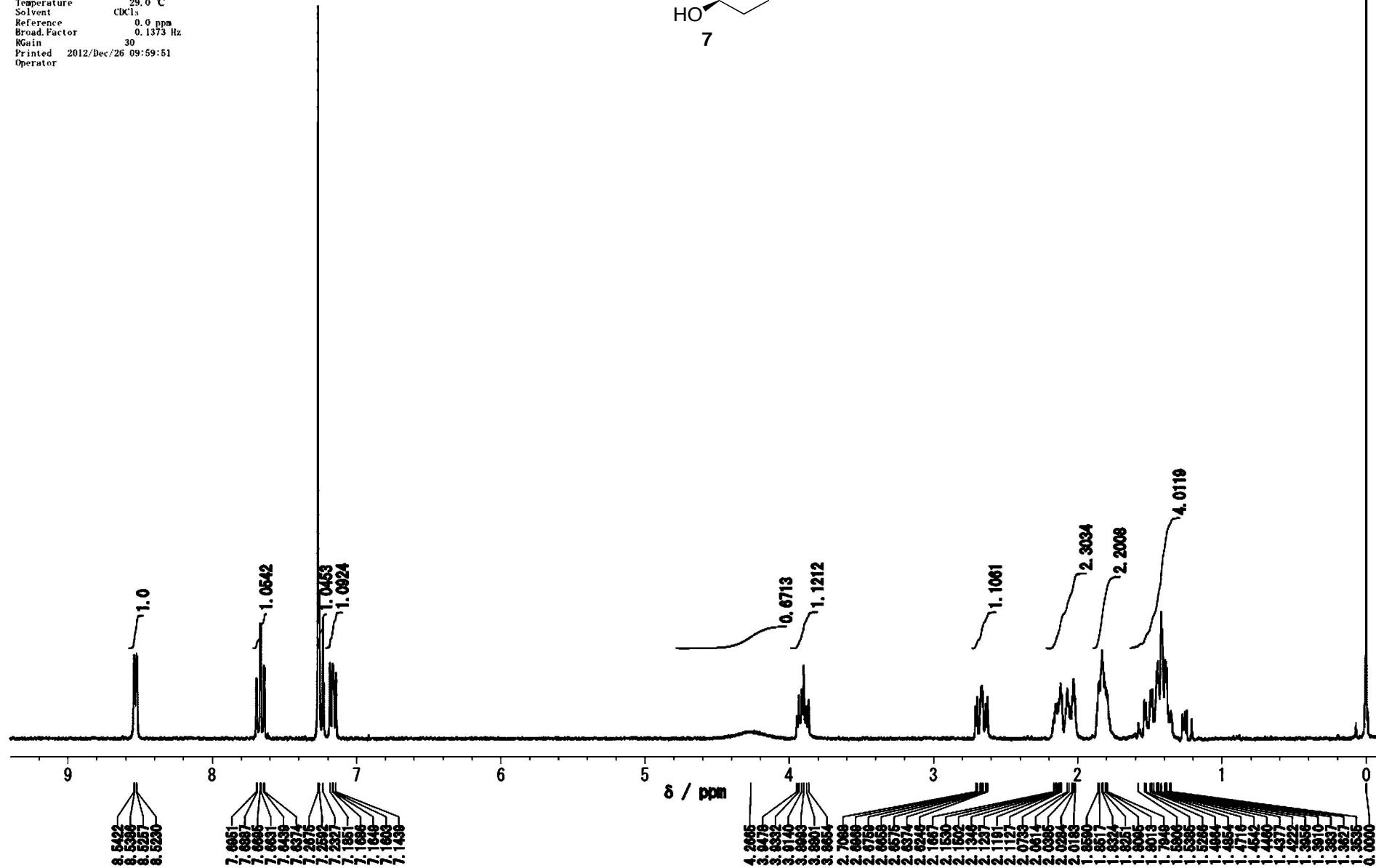
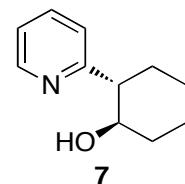
6



Date Dec 18 12

Comment STANDARD 1H OBSERVE

ObsNuc  $^1\text{H}$   
ExMode N0N  
ObsFreq 299.96 MHz  
ObsSet -1.0 kHz  
ObsFine 995.0047 Hz  
Point 16384  
Frequency (Span) 4500.45 Hz  
Scan 16  
AcqTime 3.4983 s  
PD 1.502 s  
Pulse1 6.0  $\mu\text{s}$   
Temperature 29.0  $^{\circ}\text{C}$   
Solvent  $\text{CDCl}_3$   
Reference 0.0 ppm  
Broad. Factor 0.1373 Hz  
RGain 30  
Printed 2012/Dec/26 09:59:51  
Operator



Date Dec 19 12  
 Comment  
 C13 Standard Observe  
 Stick=none Tune=6.4 Match=0.4  
 ObsNuc  $^{13}\text{C}$   
 ExMode NON  
 ObsFreq 75.43 MHz  
 ObsSet -1.0 kHz  
 ObsFine 996.3672 Hz  
 Point 32768  
 Frequency(Span) 18761.73 Hz  
 Scan 256  
 AcqTime 1.4992 s  
 PD 1.501 s  
 Pulsel 6.0  $\mu\text{s}$   
 Temperature 29.0  $^{\circ}\text{C}$   
 Solvent  $\text{CDCl}_3$   
 Reference 77.0 ppm  
 Broad.Factor 0.2863 Hz  
 RGain 30  
 Printed 2012/Dec/26 09:51:54  
 Operator

